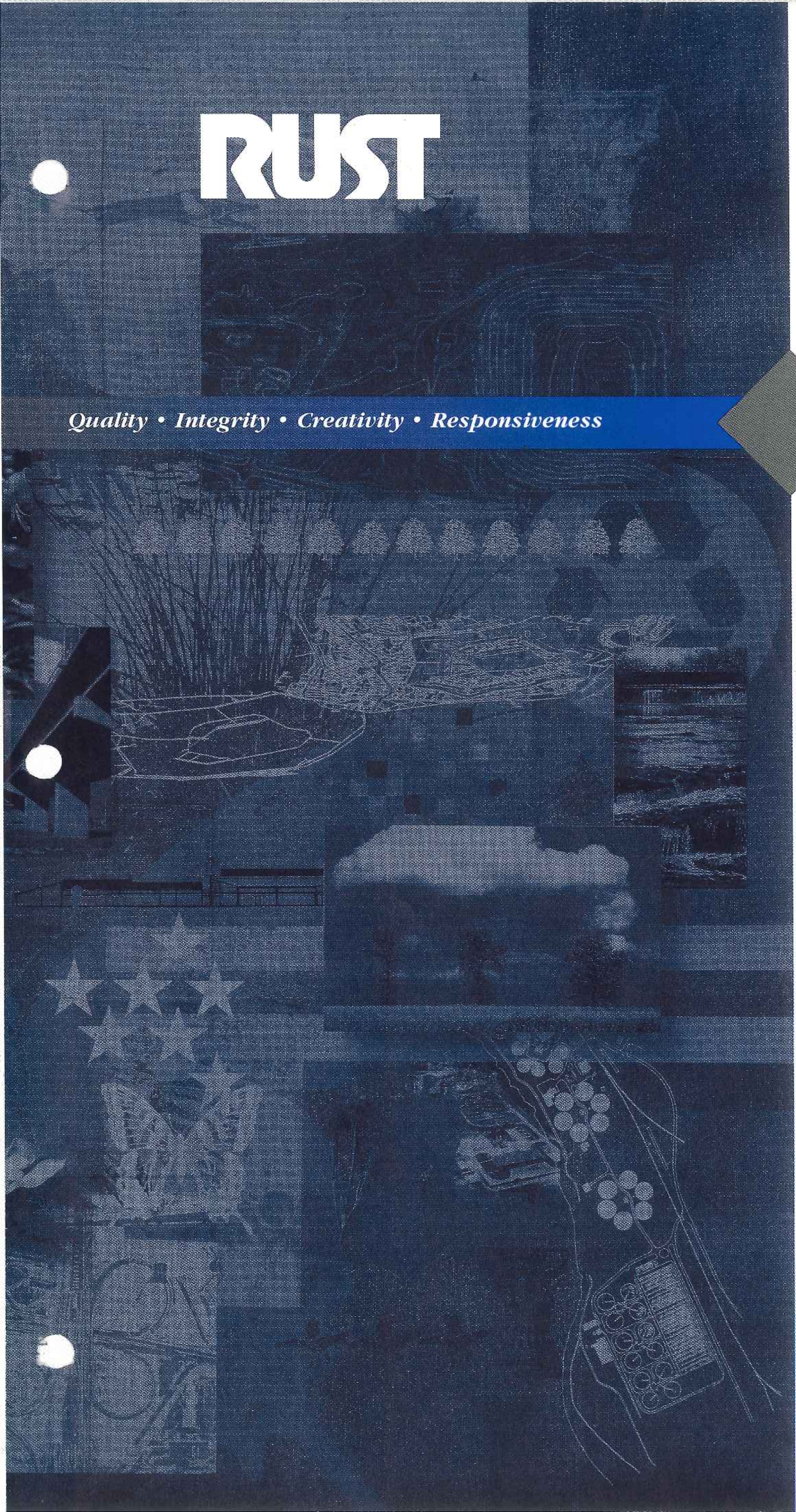


RCRA Facility Investigation (RFI) Phase I Workplan

Quality Assurance Project Plan Appendices B and C

Chemical Waste Management
Vickery, Ohio

U.S. EPA ID No.
OHD 020 273 819

Prepared for:

CWM - Vickery, Inc.

May 1996

RUST

Rust Environment & Infrastructure

APPENDIX A

SOP No.: 13.2

Title : Volatile Organics - Method 8260A

1.0 SCOPE AND APPLICATION

This method is used to identify and quantify purgeable compounds in waste water, soil, and various types of waste samples using GCMS methodology. The compounds listed below include the most common requested volatile parameters. Their respective retention time and quantitation ion are listed in Table 1 for the target compounds.

<u>Target Compound List</u>

1. Chloromethane
2. Bromomethane
3. Vinyl Chloride
4. Chloroethane
5. Methylene Chloride
6. Acetone
7. Carbon Disulfide
8. 1,1-Dichloroethene
9. 1,1-Dichloroethane
10. trans-1,2-Dichloroethene
11. Chloroform
12. 1,2-Dichloroethane
13. 2-Butanone
14. 1,1,1-Trichloroethane
15. Carbon Tetrachloride
16. Vinyl Acetate
17. Bromodichloromethane
18. 1,1,2,2-Tetrachloroethane
19. 1,2-Dichloropropane
20. trans-1,3-Dichloropropene
21. Trichloroethene
22. Dibromochloromethane
23. 1,1,2-Trichloroethane
24. Benzene
25. cis-1,3-Dicholoropropene
26. 2-Chloroethyl Vinyl Ether
27. Bromoform
28. 2-Hexanone
29. 4-Methyl-2-pentanone
30. Tetrachloroethene

31. Toluene
32. Chlorobenzene
33. Ethyl Benzene
34. Styrene
35. Total Xylenes

<u>Appendix IX List</u>

1. Acetonitrile
2. Acrylonitrile*
3. Allyl Chloride
4. 2-Chloro-1,3-butadiene
5. 1,2-Dibromo-3-chloropropane
6. Dibromomethane
7. 1,2-Dibromoethane
8. 1,2-Dichlorobenzene
9. 1,3-Dichlorobenzene
10. 1,4-Dichlorobenzene
11. trans-1,4-Dichloro-2-butene
12. Dichlorodifluoromethane
13. p-Dioxane*
14. Ethyl methacrylate
15. Isobutyl alcohol
16. Methacrylonitrile
17. Methyl iodide
18. Methyl methacrylate
19. Pentachloroethane
20. Propionitrile*
21. 1,1,1,2-Tetrachloroethane
22. Hexachloroethane
23. 1,2,4-Trichlorobenzene
24. Trichlorofluoromethane
25. 1,2,3-Trichloropropane

*Poor purging efficiency resulting in high EDL.

Additional Compounds

1. MTBE
2. 2, 2 - Dichloropropane
3. 1, 3 - Dichloropropane
4. Isopropylbenzene
5. Bromobenzene
6. n - Propylbenzene
7. 2 - Chlorotoluene
8. 4 - Chlorotoluene
9. 1, 3, 5 - Trimethylbenzene
10. tert - Butylbenzene
11. 1, 2, 4 - Trimethylbenzene
12. sec - Butylbenzene
13. 4 - Isopropyltoluene
14. n - Butylbenzene
15. Hexachlorobutadiene
16. Naphthalene
17. 1, 2, 3 - Trichlorobenzene

TABLE 1

Comp No.	Compound Name	Retention Time, Min	Quantitation Ion
1)	*Fluorobenzene (IS)	8.14	128.0
2)	Chloromethane	2.49	50.0
3)	Bromomethane	3.10	94.0
4)	Vinyl Chloride	2.61	62.0
5)	Chloroethane	3.25	64.0
6)	Acrolein	4.37	56.0
7)	Acrylonitrile	5.69	53.0
8)	Methylene Chloride	5.49	84.0
9)	Acetone	4.57	43.0
10)	Carbon Disulfide	5.24	76.0
11)	1,1-Dichloroethane	4.69	96.0
12)	trans-1,2-Dichloroethene	6.06	96.0
13)	1,1-Dichloroethane	6.75	63.0
14)	1,2-Dichloroethene (total)	7.73	96.0
15)	Chloroform	8.00	83.0
16)	1,2-Dichloroethane-d4	9.04	65.0
17)	1,2-Dichloroethane	9.18	62.0
18)	2-Butanone	7.57	72.0
19)	*1,4-Difluorobenzene (IS)	9.83	114.0
20)	1,1,1-Trichloroethane	8.63	97.0
21)	Carbon Tetrachloride	9.02	117.0
22)	Vinyl Acetate	6.98	43.0
23)	2-Chloroethylvinyl Ether	11.47	106.0
24)	Bromodichloromethane	10.77	83.0
25)	1,2-Dichloropropane	10.47	63.0
26)	cis-1,3-Dichloropropene	11.73	75.0
27)	Trichloroethene	10.24	130.0
28)	Dibromochloromethane	13.43	129.0
29)	1,1,2-Trichloroethane	12.73	97.0
30)	Benzene	9.22	78.0
31)	trans-1,3-Dichloropropene	12.55	75.0
32)	Bromoform	15.92	173.0
33)	*Chlorobenzene-d5 (IS)	14.49	117.0
34)	4-Methyl-2-Pentanone	11.61	43.0
35)	2-Hexanone	13.00	43.0
36)	Tetrachloroethene	13.30	164.0
37)	1,1,2,2-Tetrachloroethane	16.41	83.0
38)	Toluene	12.24	92.0

39)	Toluene-d8	12.14	98.0
40)	Chlorobenzene	14.55	112.0
41)	Ethylbenzene	14.75	106.0
42)	Styrene	15.61	104.0
43)	Xylene (total)	15.59	106.0
44)	Bromofluorobenzene	16.53	95.0

*Compound is Internal Standard. Compounds listed under each (IS) is quantified against that particular (IS).

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into a gas chromatograph by the purge and trap method.

2.2 An inert gas is bubbled through the solution at ambient temperature (at elevated temperatures for soil samples), and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences and contamination, under the analysis conditions, by analyzing method blanks.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph

Hewlett-Packard 5890 Gas Chromatographic Systems (GC) are employed for execution of this method. The GCs are complete with temperature programming capabilities, and all required accessories such as columns, gases, cooling valves and syringes. Sample introduction is accomplished through the use of purge and trap systems.

4.2 Purge and Trap System

The Tekmar 2000/3000 purge and trap system is coupled with the gas chromatographic system. The system is equipped with a Tekmar 2016 sixteen position autosampler, and a sample heating device for soil samples.

The purge and trap device consists of three separate modules. The sample purger, the trap and the desorber. The purging chamber accepts glass vessels capable of holding at least 5-ml of liquid samples or 5 grams of soil samples. The glass tubes are stored in an oven at 105℃ to prevent contamination from organic vapors.

The trap utilized by the laboratory is 25 cm long and has an inside diameter of 0.105 in. Traps are marketed as VOCARB 3000 by vendors such as Supelco, and consist of graphitized carbon.

A complete description of the inner workings of this purge and trap model is available in the Tekmar 2000/3000 manual.

4.3 Mass Spectrometer

The HP-5970 Quadropole Mass Selective Detector is used as the detection device for Method 8260. This system is capable of scanning from 35-260 amu every one second or less, using 70 volts (nominal) electron energy in the EI mode. After proper tuning, the system produces a mass spectrum that meets all the criteria in Table 4 when 50 ng of 4-Bromofluorobenzene (BFB) are injected into the gas chromatograph.

4.4 Data System

Each GC/MS system is attached to a dedicated 486 or pentium based computer equipped with Enviroquant software for automated acquisition and processing. The software generates total and extracted ion profiles of each compound and is capable of performing library searches on spectra using a full EPA/NIH Mass Spectral Data Library. Each system is attached to an internal laboratory computer network for additional data processing, storage and archiving.

4.5 Column

A Restek Megabore column, 60 meters in length, with a 0.53 mm internal diameter and 2.0 micron film thickness is used.

4.6 Microsyringes - 10 ul, 25 ul, 100 ul, 250 ul, 500 ul, and 1000 ul.

4.7 Luerlock syringe - 5 and 25 ml gas tight.

5.0 REAGENTS

5.1 Organic free reagent water.

5.2 Stock solutions.

5.3 Methanol, High purity grade, B & J Brand for Purge and Trap analysis.

6.0 PROCEDURE

6.1 Calibration

Five concentration levels are analyzed for each analyte and surrogate standards. A five point curve is then created after all 5 points are analyzed. Calibration levels are analyzed at 20, 50, 100, 150 and 200ug/l for all analytes and surrogate standards except for 2-Chloroethyl vinyl ether which is analyzed at 40, 100, 200, 300 and 400ug/l.

6.2 Instrumentation Parameters

The following set of operating conditions exist for method 8260A.

Electron energy:	70 volts (nominal)
Mass range:	35-260 amu
Scan time:	To give 5 scans/peak but not to exceed 7 sec/scan

Initial column temperature:	10^{o} C
Initial column holding time:	4 min
Column temperature program:	8^{o} C/minutes
Final column temperature:	190^{o} C
Final column holding time:	1 min
Injector temperature:	220^{o} C
Source temperature:	According to manufacturer's specifications
Transfer line temperature:	280^{o} C (Preset to manufacturer)
Carrier gas:	Helium at about 8ml/min

6.3 Tuning

At the beginning of each day, each GC/MS system is injected with 50ng of BFB and tuned to meet the criteria listed in Table 4. The analysis must not commence unless the criteria are met. This requirement must be met for each 12 hour interval.

6.4 Calibration Requirements

Once tuning requirements are met, the initial or continuing calibration check must be established. The generation of response factors is the next step in establishing the calibration requirements for method 8260A. The instructions for determining the response factors are as follows:

> Tabulate the area response of the quantitation ions (see Table 1) against the concentration for each compound and each internal standard. Calculate response factors (RF) for

each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard with the retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = \frac{(A_x)\ (C_{is})}{(A_{is})\ (C_x)}$$

where:

A_x - Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_x = Concentration of the compound being measured.

The average RF must be calculated for each compound. A system performance check should be completed before the calibration curve is used. Five compounds, the System Performance Check Compounds, or SPCCs, are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene (see Table 4). The minimum relative response factors for these compounds should be 0.1, 0.1, >0.1, 0.3 and 0.3. These compounds typically have RFs respectivly, of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Initial calibration is analyzed at 5 levels. These levels are 20, 50, 100, 150 and 200ug/l. The following compounds have higher initial calibration levels.

Acrolein	80	200	400	600	800
Acrylonitrile	80	200	400	600	800
2 - Chloroethyl Vinyl Ether	40	100	200	300	400

Using the RFs from the initial calibration, calculate the percent relative standard deviation (% RSD) for all compounds.

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \times 100$$

where:

RSD	=	relative standard deviation
$\bar{X}$	=	mean of 5 initial RFs for a compound
N	=	Number of calibration points
SD	=	standard deviation of average RFs for a compound
X_i	=	Response factor for each point

$$SD = \left[\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1} \right]^{1/2}$$

The % RSD for each individual analyte should be less than 30 percent for the calibration check compounds (CCCs) (see Table 3). This criterion must be met in order for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride

The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a 50 ppb calibration standard and checking the SPCC and CCC.

System Performance Check Compounds (SPCCs) - A system performance check must be completed each 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Potential problems include standard mixture degradation, injection port inlet contamination, contamination of the front end of the analytical column, and active sites in the column or chromatographic system.

Calibration Check Compounds (CCCs) -

$$\% \text{ Difference} = \frac{\overline{RF_I} - RF_C}{\overline{RF_I}} \times 100$$

where:

$\overline{RF_I}$ = average response factor from initial calibration

RF_C = response factor from current verification check standard

If the percent difference for any compound is greater than 20, the laboratory should consider this observation as a warning limit. If the percent difference for each analyte is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (< 25% difference), for any one analyte, corrective action MUST be initiated. If the source of the problem cannot be determined following the initiation of the corrective action, a new five-point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins.

The internal standard response and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. Tables 3 and 4 list SPCC and CCC compounds.

6.5 Retention Time Change

If the retention time for any internal standard changes by more than 30 sec. from the last check calibration or when an internal standard area changes by a factor of 2 (-50% to +100%), from the last continuing calibration standard, then all affected samples must be reanalyzed after the problem is corrected. Typical retention times for 8260A analytes under the parameters listed in Section 6.2 is provided on Table 1.

6.6 Qualitative Analysis

6.6.1 The compounds listed in Section 1 shall be identified by an analyst by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identification.

6.6.1.1 Relative relation time of the sample and standard must agree ± 0.05.

6.6.1.2 Correspondence of the sample component and standard component mass spectra.

6.6.2 The requirement for qualitative verification by comparison of mass spectra are as follows:

All ions present in the standard mass spectra at a relative intensity greater than 10% must be present in the sample spectrum. All ions specified must agree within ± 20% between the standard and sample spectra. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for.

6.7 Quantitative Analysis

When a compound is identified, quantification is based on the integrated abundance of the primary characteristics ion and the response and amount of the corresponding internal standard.

$$\text{Concentration (ug/L)} = \frac{(Ax)\ (Is)\ (D)}{(Ais)\ (Avg\ RF)\ (Vo)}$$

$$\text{Concentration (ug/kg)} = \frac{(Ax)\ (Is)\ (D)}{(Ais)\ (Avg\ RF)\ (W)\ (S)}$$

where,

Ax	=	Area of primary ion
Is	=	Amount of internal standard, ug/L
Ais	=	Area of ion for internal standard
Avg RF	=	Mean relative response factor for compound measured
Vo	=	Volume of sample purged, L
D	=	Dilution factor
W	=	Weight in Kg
S	=	Solid

6.8 For non-TCL components, a library search may be executed. Up to 20 non-surrogate organic compounds shall be tentatively identified when required. Guidelines for making tentative identification:

6.8.1 Ions greater than 10% of the most abundant ion should be present in the sample spectrum.

6.8.2 Relative intensities of the major ions should agree within ± 20%.

6.8.3 Molecular ion present in the reference spectrum should be present in sample spectrum.

6.8.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

6.9 GC/MS Analysis

6.9.1 Water Samples

6.9.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

6.9.1.3 BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples.

6.9.1.4 Adjust the purge gas (Helium) flow rate to approximately 40ml/min on the purge and trap device.

6.9.1.5 Remove the plunger from a 5ml syringe. Open the sample and carefully pour the sample into the syringe barrel to just short of overflowing. Compress the sample. Vent any residual air while adjusting the sample volume to 5.0ml.

6.9.1.6 Add 5.0ul of surrogate spiking solution and 5ul of internal standard solution (50 ppm each) through the valve bore of the syringe.

6.9.1.7 For the matrix spike analysis, add 5ul of the matrix spike solution (50 ppm) to the sample to be purged. This will yield a final concentration of 50ug/L (ug/kg for soils) in the final sample.

6.9.1.8 The samples are analyzed with appropriate dilution when the concentration level of any analyte exceeds the calibration range. Dilutions are made in the 5ml gastight luer lock syringe by adding reagent water. Calculate the volume of reagent water needed for the dilution and add into a 4ml syringe. Using a suitable syringe, add the exact volume of sample into the reagent water in the 5ml syringe. Add 5ul of Internal Standard & Surrogate and analyze as discussed above.

If the dilute sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

6.9.1.10 The spiked sample is injected into a purging tube attached to the Purge & Trap device. Purge the sample for 11 minutes and desorb the contents of the trap at 200^{o} for 2 minutes into the GC/MS.

6.9.1.11 Low Concentration Method: This method is applicable to water samples containing low levels of contaminants. The detection limits are generally improved by analyzing larger sample volume (25 ml). The detection limits of compounds with poor purging efficiency (such as ketones) do not significantly improve when low concentration method is utilized. The low concentration analytical procedure is virtually the same as low level water analysis except for concentration of the calibration, surrogate and internal standards. The following concentration levels and ranges are analyzed:

Calibration	-	2, 5, 20, 50, 80	ug/L
Surrogates	-	2, 5, 20, 50, 80	ug/L
		20 in sample and QC	ug/L
Internal Standards	-	20	ug/L
Matrix Spike/LCS	-	20	ug/L
Continuing Calibration	-	20	ug/L

Acceptance criteria for the initial and continuing calibrations is based on the evaluation of check compounds exclusively (Table 3). Criteria for percent RSD and difference in the initial and continuing calibrations are described in section 6.4. System performance check compounds are not monitored for low concentration method.

6.9.2 Sediment/Soil and Waste Samples

6.9.2.1 Low Concentration method: Applicable for samples containing individual compounds of <1mg/kg. All granular/porous waste/sediment/soil samples can be analyzed using this method.

Weigh 5g of the sample into a glass sparge tube and record the weight to the nearest 0.1g. Add reagent water to a 5ml luerlock type syringe and adjust the volume to 5ml. Add 5ul of internal standard and 5ul of surrogate standard to the water. Connect the sparge tube with the sample to the purge & trap device and add the spiked water to the sample. Heat the sample to 40℃ ±1℃ and purge the sample for ul minutes. Desorb the trap at 200c for 2 minutes into the GCMS.

If the concentration level of any analyte exceeds the calibration range and is below 1mg/kg, the sample should be analyzed by weighing 1g of the sample. If the concentration level of any analyte is higher than 1mg/kg, then the high concentration method should be used.

6.9.2.2 High Concentration Method: The method is based on extracting the soil/sediment with methanol. Weigh 4gm of the sample into a 20ml vial using a top loading balance. Record the weight to the nearest 0.1g. Using a pipet, add 10.0ml methanol into the vial. Close the cap and shake for 2 minutes. 100ul of the extract is added to reagent water collected in a 5ml luerlock syringe. 5ul each of Internal Standard and Surrogate are added to the syringe. Proceed with the analysis as outlined in the water sample analysis. If further dilution is needed, a smaller extract volume is used and the same procedure is repeated.

A separate method blank containing 100ul methanol should be analyzed prior to a high concentration sample analysis and should be free of contaminants.

6.9.2.3 Samples extracted through Toxicity Characteristic Leachate Procedure by zero headspace extractor are analyzed by this method. Only those compounds designated by the TCLP method are accounted for. Samples are analyzed at 10 times dilution in order to minimize the effects of acetic acid on the chromatography and purge and trap systems. TCLP compounds are listed on Table 7.

7.0 QUALITY CONTROL

7.1 Prior to initiating on going data, it is necessary that the GC/MS meets BFB abundance criteria (Table 5) every twelve (12) hour period for the method.

7.2 When twelve (12) hours have elapsed since the initial tune, the GC/MS must be retuned to continue the analysis.

7.3 If the retention time of the standard changes by more than 30 seconds, the GC system must be inspected for malfunction.

7.4 Surrogate recoveries must be evaluated by determining whether the concentrations fall inside the required recovery limits listed in Table 6.

7.5 A matrix spike and spike duplicate must be performed every 20 samples at the concentration equal to mid-level calibration (50ug/l). Table 2 lists the matrix spike compounds, concentration added, recovery limits and %RPD for soil and water matrices. TCLP samples are spiked with TCLP target compounds at 50ug/l concentration (see Table 7).

7.6 A method blank must be performed for each 12 hour time period.

7.6.1 A method blank for volatile analysis must contain less than or equal to 5 times the CRQL of methylene chloride, acetone, toluene and 2-butanone.

7.6.2 For all other target compound list not listed above, the method blank may contain less than or equal to the CRQL of any single analyte.

7.7 Lab Control Spikes (LCS) are analyzed per batch or every 20 samples whichever comes first. LCS compounds and their concentrations are listed on Table 8. Recovery limits listed are advisory.

8.0 SAFETY

8.1 Safety glasses, laboratory coats, and latex gloves must be worn.

8.2 Due to the toxicity or carcinogenicity of each reagent, each chemical compound should be treated as a potential health hazard.

8.3 Material Safety Data Sheets (MSDS) can be found on the procurement bookshelves located in the administrative area.

8.4 Standard preparation should be handled under a hood.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition

TABLE 2

MATRIX SPIKE COMPOUNDS	CONC. ADDED	WATER	%RPD	SOIL/SEDIMENT	%RPD
		ACCEPTABLE RECOVERY RANGES			
1,1-Dichloroethene	50	61-145	14	59-172	22
Trichlorethene	50	71-120	14	62-137	24
Chlorolenzene	50	75-130	11	60-133	21
Toluene	50	76-125	13	59-139	21
Benzene	50	76-127	13	66-142	21

TABLE 3

CALIBRATION CHECK COMPOUNDS

1 - 1,1-Dichloroethene

2 - Chloroform

3 - 1,2-Dichloropropane

4 - Toluene

5 - Ethylbenzene

6 - Vinyl chloride

TABLE 4

SYSTEM PERFORMANCE CHECK COMPOUNDS

1 - Chloromethane

2 - 1,1-Dichloroethane

3 - Bromoform

4 - 1,1,2,2-Tetrachloroethane

5 - Chlorobenzene

TABLE 5

BFB KEY ION ABUNDANCE CRITERIA

Mass	Ions Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 6
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

SURROGATE COMPOUND	LOW/MEDIUM WATER	LOW/MEDIUM SOIL/SEDIMENT
4-Bromofluorbenzene	86-115	74-121
1,2-Dichlorodthane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117
1,2 - Dichloroborzone - d_2		

TABLE 7

TCLP Matrix Spike Recovery

Compound	Spike Added (ug/L)	% Recovery Lower Limit	% Recovery Upper Limit
Vinyl Chloride	50	50	125
1,1-Dichloroethene	50	50	125
Chloroform	50	50	125
1,2-Dichloroethane	50	50	125
2-Butanone	50	50	125
Carbon Tetrachloride	50	50	125
Trichloroethene	50	50	125
Benzene	50	50	125
Tetrachloroethene	50	50	125
Chlorobenzene	50	50	125

TABLE 8

Lab Control Std Recovery for Soil and Water

Compound	LCS Added	% Recovery Lower Limit	% Recovery Upper Limit
Vinyl Chloride	50	50	125
1,1-Dichloroethene	50	50	125
Chloroform	50	50	125
1,2-Dichloroethane	50	50	125
1,1,1-Trichloroethane	50	50	125
Carbon Tetrachloride	50	50	125
Bromodichloromethane	50	50	125
Trichloroethene	50	50	125
Dibromochloromethane	50	50	125
Benzene	50	50	125
Bromoform	50	50	125

Units in ug/L or ug/Kg

Effective Date:	April 1996
Version Number:	3
Initiated By :	Marty Snodgrass
Approved By :	[illegible]
	[illegible]

SOP No.: 13.34

Title : SOP for Method SW 8270B
GC/MS Analysis of The Target Compound List and Appendix IX Semivolatile Organics

1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) describes the methodology used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and water. Table 1 indicates Target Compound List (TCL) typically determined by this method and lists the method suggested detection limits for water and soil. Table 2 lists the Appendix IX compounds which can be determined using 8270 methodologies.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation methods.

3.0 INTERFERENCE

3.1 GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference originated from the preparation of the samples and initiate the corrective action to eliminate the problem.

3.2 Contamination caused by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between each use.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph/Mass Spectrometer

Hewlett Packard 5970 MSD System equipped with an autosampler is utilized. The HP 5970 MSD is a complete instrument composed of two modules: a Controller and a main frame GCMS.

4.2 Columns

A 30 meter 0.25 mm ID, 1.01 meter RTX-5 (5% phenyl methyl silicon) Restek column is used.

4.3 Syringe: 10 ll

5.0 GC CONDITION

5.1 The following GC parameters are established:

- Injection port temp 280℃
- Interface temp 300℃
- Initial temp 40^{oC}
- Initial time 4 min
- Rate at 15℃ per min
- Final temp 310℃
- Final time 20 min
- Equilibrium time .5 min
- Septum purge flow on at .5 ml/min
- Septum purge flow on at .5 min
- Flow rate at about 0.7 ml/min
- Splitless flow about 50 ml/min
- Injection type "Splitless"
- Autosampler injection mode "Fast"
- Sample Volume 1 ll.

5.2 GC/MS CONDITION

5.2.1 Scanning from 35 to 500 amu in less than 1 second, using 70 volt (nominal) electron energy in the Electron Impact Ionization mode. Scan delay is past solvent peak or ends in approximately 7 minutes.

5.2.2 GCMS Tuning - to determine the system performance, 50 ng of decafluorotriphenylphosphine (DFTPP) is injected and the mass spectrum is evaluated. The following criteria must be met before any further analysis is performed.

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

MASS	ION ABUNDANCE CRITERIA
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
365	>1% of mas 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

5.3 CALIBRATION

5.3.1 Upon satisfactory completion of DFTPP analysis, five levels of calibration standards at 20, 50, 80, 120 and 160 ng are analyzed. Calibration standards must contain the following internal and surrogate standards. Appendix IX calibration standards are also analyzed at 20, 50, 80, 120 and 160ng, except for those compounds with low instrument sensitivities. Calibration for poor sensitivity compounds are performed with the exclusion of the 20ng standard.

5.3.1.1 Internal Standards - the following Internal Standards at 401g/ml must be present in the Calibration Standard.

- 1,4-dichlorobenzene-d_4
- Naphthalene-d_8
- Acenaphthane-d_{10}
- Phenanthrene-d_{10}
- Chrysene-d_{12}

- Penylene-d_{12}

5.3.1.2 The following Surrogate Standards at 20, 50, 80, 120 and 160 ng are analyzed.

- Phenol-d_6
- 2-Fluorophenol
- 2,4,6-Tribromophenol
- nitrobenzane-d_5
- 2-fluorobiphenyl
- p-terphenyl-d_{14}

5.4 After analyzing the initial Calibration Standard the average RF (Response Factor) should be calculated for each compound. The percent relative standard deviation (% RSD) should be calculated for each compound. Calibration Check Compounds (CCC) must have a % RSD less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative time units. System performance check compounds must have a minimum RF of 0.05. The CCC and SPCC compounds are listed as follow:

SPCC	CCC
N-nitroso-di-n-prophylanine	Acenaphthene
hexachlorocyclopantachiene	1,4-Dichlorobenzene
2,4-dinitrophenol	N-Nitroso-di-nphenylamine
4-nitrophenol	Di-n-octylphthalate
	Fluorantane
	Benzo(a)pyrane
	4-chloro-3-methylphenol
	2,4-Dichlorophenol
	2-Nitrophenol
	Phenol
	Pentachlorophenol
	2,4,6-Trichlorophenol

5.5 Internal Standard responses and retention times in the calibration check, blanks and samples must be evaluated. Retention time variation for any internal standard must be less than 30 seconds from the 12 hour calibration check. Variation of the areas for internal standards must not vary by more than a factor of two or -50% to +100%.

5.6 A continuing calibration (daily) at 50 ng concentration containing all semivolatile analytes, including all required surrogates must be analyzed every 12 hours. The following criteria must be met before sample analysis begins:

- CCC < 30% RSD

- SPCC $\geq$ 0.050 RF

- Internal Standard Area -50 to +100%

- Retention time for Internal Standards $\pm$ 30 seconds

6.0 SAMPLE ANALYSIS

6.1 Initially 0.5 ml of Acid and Base Neutral extracts are combined and 10 ul of 4000 ug/ml internal standard is added to each mix. One ul of this extract is injected into the GCMS using the same parameters as the calibration standard. All samples must be injected within a 12 hour period starting with the analysis of DFTPP.

6.2 Qualitative Analysis

6.2.1 Two criteria must be satisfied to verify compound identification

6.2.1.1 Elution of sample component at the same GC relative retention time (RRT) $\pm$0.06 units. Table 3 lists typical retention times for target analytes.

6.2.1.2 Correspondence of the sample component and the standard component mass spectrum.

All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum. The relative intensity of these ions must agree $\pm$ 20% between the standard and sample spectra.

6.2.2 Library Search

6.2.2.1 When required, a search may be performed for the purpose of tentative identification. Only after performing a visual comparison of the sample spectra with the nearest library searches will the analyst assign a tentative identification. The analyst should use an approach similar to the 5 step identification listed for method SW 8270 (pp-18), Sept 1986.

6.3 Quantitative Analysis

6.3.1 When a compound is identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation is based on the internal standard technique. The internal standard nearest the retention time of that given analyte, shall be used. Table 3 lists the quantitation ions for target analytes and GC compounds.

7.0 CALCULATIONS

The following information should be used throughout the quantitation process.

7.1 Response Factor

$$RF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

Where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard

C_x = Concentration of the compound being measured (ug/ml)

C_{is} = Concentration of the specific internal standard (ug/ml)

7.2 % RSD and % Difference

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Average RF}} \text{ X } 100$$

$$\% \text{ difference} = \frac{\text{AvgRF}_i \text{ (initial calibration)} - \text{RF}_c \text{ (Continuing calibration)} \text{ X100}}{\text{Avg RF}_I}$$

7.3 Sample Calculation

$$\text{Water Concentration ug/l} = \frac{(A_x)(I_s)(V_t)(Dil)}{(A_{is})(RF)(V_o)(V_i)}$$

$$\text{Soil concentration ug/kg} = \frac{(A_x)(I_s)(V_t)(Dil)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

Where:

I_s = Amount of internal standard injected (ng)

V_t = Volume of total extract

V_o = Initial volume

V_i = Volume of extract injected (ml)

W_s = Weight of sample extracted (G)

D = Percent solids

Dil = Dilution applied

7.4 Low Concentration Method

This method is applicable to soil and water samples containing low level contaminants and minimal matrix interferences. To achieve lower detection limits, final volume of the sample extracts are brought to 0.5 ml. Concentrations of surrogate and internal standards should be adjusted in order to produce levels comparable to low level procedure. Quality control and recovery ranges should not be affected by final volume reduction. Low level quality control criteria is applicable to this modified procedure.

8.0 QUALITY CONTROL

8.1 Blank analysis - A method blank is analyzed with each analytical batch to examine the interferences and contamination from extraction and analysis. Concentration of the target compounds in the blank must be less than or equal to the PQL except for phthalate esters which can be 5 times the PQL. If the above criteria are not met, reinjection or reextraction of the blank and the samples is required.

8.2 Surrogate analysis - Surrogate standard determinations are performed on all samples and blanks. The following range of recoveries is considered to be the Q.C. limits.

SURROGATE COMPOUND	WATER	LOW/MEDIUM SOIL/SEDIMENT
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

If recoveries of 2 surrogates in either the BN or acid fraction are outside the surrogate spike recovery limits, or recovery of any one surrogate in either the BN or Acid is below 10%, corrective action should be taken. First, re-inject the sample if no improvement is observed, reextraction should be considered.

8.3 Matrix Spikes - A matrix spike and matrix spike duplicate are analyzed with each case of 20 samples. Recoveries of MS/MSD should be calculated and listed. The following range of recoveries are suggested:

MATRIX SPIKE RECOVERY LIMITS

FRACTION	MATRIX SPIKE COMPOUND	AMOUNT ADDED (ug)	WATER	SOIL/ SEDIMENT
BN	1,2,4-Trichlorobenzene	100	39-98	38-107
BN	Acenaphthene	100	46-118	31-137
BN	2,4-Dinitrotoluene	100	24-96	28-89
BN	Pyrene	100	26-127	35-142
BN	N-Nitroso-Di-n-Prophylamine	100	41-116	41-126
BN	1,4-Dichlorobenzene	100	36-97	28-104
Acid	Pentachlorophenol	200	9-103	17-104
Acid	Phenol	200	12-89	26-90
Acid	2-Chlorophenol	200	27-132	25-102
Acid	4-Chloro-3-Methylphenol	200	23-97	26-103
Acid	4-Nitrophenol	200	10-80	11-114

When TCLP samples are analyzed matrix spike must include all TCLP compounds at 100ug/ml. Table 6 lists both TCLP matrix spike compounds and recovery ranges.

8.4 Lab Control Sample

8.4.1 A laboratory control sample is extracted and analyzed routinely with each extracted batch. Calculated concentrations are compared with the amount of spiked compound added. The results are used for in house Q.C. monitoring of both the extraction and analytical processes. It is not necessary to report LCS results in a CLP data package, however, other types of data packages may require submittal of the results. Tables 4 and 5 lists the spiked LCS compounds, concentrations added and recovery ranges for soil and water matrices. Table 7 lists the LCS compounds used for TCLP batches. The recovery ranges for TCLP LCS are advisory.

8.5 Internal Standard Recoveries and Retention times - when internal standard recoveries (-50 to +100%) or retention time requirements, (0.06 RRT) are not satisfied, the sample is reinjected and reanalyses results are submitted if acceptable. If both analyses do not meet the criteria, then both results are submitted. Table 3 lists the internal standards and the associated target surrogate compounds.

8.6 All extracts must be analyzed within 40 days after completion of extraction.

8.7 Dilutions are performed on samples when the concentration of target analytes exceeds the calibration range. Additional IS must be added to the diluted extract to maintain the required IS concentration. Surrogate recoveries (if possible) are not required to fall within the suggested ranges.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW846, 3rd Edition

TABLE 1

Target Compound List (TCL) and
Practical Quantitation Limits (CRQL)

Semivolatiles	CAS Number	Quantitation Limits Water ug/L	Low Soil/Sediment ug/Kg
Phenol	108-95-2	10	330
bis (2-Chloroethyl) ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
bis (2-Chloroisopropyl) ether	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-dipropylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
bis (2-Chloroethoxy) methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	10	330
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	50	1600

TABLE 1 (Cont)

Target Compound List (TCL) and
Practical Quantitation Limits (CRQL)

Semivolatiles	CAS Number	Quantitation Limits Water ug/L	Low Soil/Sediment ug/Kg
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethylphthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
2,6-Dinitrotoluene	606-20-2	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl-phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-nitrosodiphenylamine	86-30-6	10	330
4-Bromophenyl-phenylether	101-55-3	10	330
Hexachlorobenze	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Di-n-butylphthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Pyrene	129-00-0	10	330
Butylbenzylphthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	20	660

TABLE 1 (Cont)

Target Compound List (TCL) and
Practical Quantitation Limits (CRQL)

Semivolatiles	CAS Number	Quantitation Limits Water ug/L	Low Soil/Sediment ug/Kg
Benzo(a)anthracene	56-55-3	10	330
Chrysene	218-01-9	10	330
bis (2-Ethylhexyl) phthalate	117-81-7	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno (1,2,3-cd) pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330

TABLE 2

Appendix IX Compounds

1. Acetophenone
2. 2-Acetylaminofluorene
3. 4-Aminobiphenyl
4. Aniline
5. Chlorobenzilate
6. 4-Chlorophenyl phenyl ether
7. m-Cresol
8. Dimethoate
9. 4-Dimethylaminoazobenzene
10. 7,12-Dimethylbenz(a)anthracene
11. 3,3'-Dimethylbenzidine
12. a,a-Dimethylphenethylamine
13. 1,3-Dinitrobenzene
14. Diphenylamine
15. 1,4-Dioxane
16. Famphur
17. Hexachloropropene
18. Isodrin
19. Isosafrole(cis)
20. Kepone
21. Methapyrilene hydrochloride
22. 3-Methylcholanthrene
23. Methyl methane sulfonate
24. 1,4-Naphthoquinone
25. 1-Naphthylamine
26. 2-Naphthylamine
27. 4-Nitroquinoline-1-oxide
28. N-Nitrosodi-n-butylamine
29. N-Nitrosodiethylamine
30. N-Nitrosodimethylamine
31. N-Nitrosomethylethylamine
32. N-Nitrosomorpholine
33. N-Nitrosopiperidine
34. N-Nitrosopyrrolidine
35. 5-Nitro-o-toluidine
36. Pentachlorobenzene
37. Pentachloronitrobenzene
38. Phenacetin
39. 1,4-Phenylenediamine
40. Phorate
41. 2-Picoline
42. Pronamide
43. Pyridine
44. Safrole
45. 1,2,4,5-Tetrachlorobenzene
46. 2,3,4,6-Tetrachlorophenol
47. Thionazin
48. o-Toluidine
49. O,O,O-Triethylphophorothioate
50. sym-Trinitrobenzene
51. Methyl methacrylate
52. Ethyl methacrylate
53. Ethyl methane sulfonate
54. o-Anisidine
55. p-Cresidine
56. 5-Chloro-2-methylaniline
57. Phthalic anlydride
58. 2,4-Diaminotoluene
59. 1-Chloronaphthalene
60. Diallate
61. Disulfoton
62. Methylparathion
63. Ethylparathion
64. 4-Aminoazobenzene
65. 4,4-Oxydianiline
66. 3,3-Dimethoxybenzidine
67. Tetraethyldithiopyrophosphate

Table 3

Compound Name	Retention Time	Quant Ion
1) *1,4-Dichlorobenzene-d4	10.48	152.0
2) Pyridine	5.70	79.0
3) N-nitrosodimethylamine	5.66	74.0
4) 2-Fluorophenol	8.32	112.0
5) Phenol-d5	9.87	99.0
6) Phenol	9.89	94.0
7) bis(2-Chloroethyl)ether	9.95	93.0
8) 2-Chlorophenol	10.17	128.0
9) 1,3-Dichlorobenzene	10.42	146.0
10) 1,4-Dichlorobenzene	10.50	146.0
11) Benzyl alcohol	10.70	108.0
12) 1,2-Dichlorobenzene	10.82	146.0
13) 2-Methylphenol	10.91	108.0
14) bis(2-Chloroisopropyl)ether	10.97	45.0
15) 4-Methylphenol + 3-Methylphenol	11.15	108.0
16) N-Nitroso-di-n-propylamine	11.21	70.0
17) Hexachloroethane	11.37	117.0
18) *Naphthalene-d8	12.72	136.0
19) Nitrobenzene-d5	11.46	82.0
20) Nitrobenzene	11.50	77.0
21) Isophorone	11.90	82.0
22) 2-Nitrophenol	12.05	139.0
23) 2,4-Dimethylphenol	12.07	122.0
24) Benzoic acid	12.27	105.0
25) bis(2-Chloroethoxy)methane	12.23	93.0
26) 2,4-Dichlorophenol	12.47	162.0
27) 1,2,4-Trichlorobenzene	12.64	180.0
28) Naphthalene	12.76	128.0
29) 4-Chloroaniline	12.84	127.0
30) Hexachlorobutadiene	13.04	224.8
31) 4-Chloro-3-methylphenol	13.65	107.0
32) 2-Methylnaphthalene	13.98	142.0
33) *Acenaphthene-d10	15.90	164.0
34) Hexachlorocyclopentadiene	14.37	236.8
35) 2,4,6-Trichlorophenol	14.49	196.0
36) 2,4,5-Trichlorophenol	14.57	196.0
37) 2-Chloronaphthalene	14.86	162.0
38) 2-Fluorobiphenyl	14.63	172.0
39) 2-Nitroaniline	15.04	138.0
40) Dimethylphthalate	15.37	163.0
41) Acenaphthylene	15.61	152.0
42) 2,6-Dinitrotoluene	15.51	165.0
43) 3-Nitroaniline	15.04	138.0

Table 3 (Cont)

Compound Name	Retention Time	Quant Ion
44) Acenaphthene	15.96	153.0
45) 2,4-Dinitrophenol	15.96	184.0
46) 4-Nitrophenol	16.00	109.0
47) Dibenzofuran	16.22	168.0
48) 2,4-Dinitrotoluene	16.22	165.0
49) Diethylphthalate	16.61	149.0
50) 4-Chlorophenyl-phenylether	16.79	204.0
51) Fluorene	16.85	166.0
52) 4-Nitroaniline	16.87	138.0
53) 2,4,6-Tribromophenol	17.30	329.6
54) *Phenanthrene-d10	18.53	188.0
55) 4,6-Dinitro-2-methylphenol	16.96	198.0
56) N-Nitrosodiphenylamine	17.00	169.0
57) 1,2-Diphenylhydrazine	17.08	77.0
58) 4-Bromophenyl-phenylether	17.65	248.0
59) Hexachlorobenzene	17.97	283.8
60) Pentachlorophenol	18.26	265.8
61) Benzidine	18.34	184.0
62) Phenanthrene	18.57	178.0
63) Anthracene	18.65	178.0
64) Carbazole	18.89	167.0
65) Di-n-butylphthalate	19.46	149.0
66) Fluoranthene	20.72	202.0
67) *Chrysene-d12	23.48	240.0
68) Pyrene	21.15	202.0
69) Terphenyl-d14	21.32	244.0
70) Butylbenzylphthalate	22.15	149.0
71) 3,3'-Dichlorobenzidine	23.27	252.0
72) Benzo(a)anthracene	23.44	228.0
73) Chrysene	23.54	228.0
74) Bis(2-Ethylhexyl)phthalate	23.25	149.0
75) *Perylene-d12	27.94	264.0
76) Di-n-octylphthalate	24.76	149.0
77) Benzo(b)fluoranthene	26.51	252.0
78) Benzo(k)fluoranthene	26.60	252.0
79) Benzo(a)pyrene	27.74	252.0
80) Indeno(1,2,3-cd)pyrene	33.26	276.0
81) Dibenz(a,h)anthracene	33.28	278.0
82) Benzo(g,h,i)perylene	34.87	276.0

*Compound is Internal Standard. Compound listed under each Internal Standard is quantified against that Internal Standard.

Table 4

Lab Control Spike for Water

Compound	Amount Added (ug)	LQL	UQL
1,2,4-Trichlorobenzene	100	55	112
Acenaphthene	100	63	101
2,4-Dintrotoluene	100	63	112
Pyrene	100	61	125
N-Nitroso-Di-n-Propylamine	100	61	102
1,4-Dichlorobenzene	100	55	101
Pentachlorophenol	200	52	144
Phenol	200	49	105
2-Chlorophenol	200	55	95
4-Chloro-3-Methylphenol	200	52	120
4-Nitrophenol	200	48	140

LQL = Lower QC Limit
UQL = Upper QC Limit

Table 5

Lab Control Spike for Soil

Compound	Amount Added (ug)	LQL	UQL
1,2,4-Trichlorobenzene	100	19	100
Acenaphthene	100	27	96
2,4-Dintrotoluene	100	21	118
Pyrene	100	21	117
N-Nitroso-Di-n-Propylamine	100	11	121
1,4-Dichlorobenzene	100	(D)	109
Pentachlorophenol	200	6	155
Phenol	200	20	81
2,Chlorophenol	200	8	92
4-Chloro-3-Methylphenol	200	28	96
4-Nitrophenol	200	8	143

LQL = Lower QC Limit
UQL = Upper QC Limit
(D) = Detected

Table 6

TCLP Matrix Spike

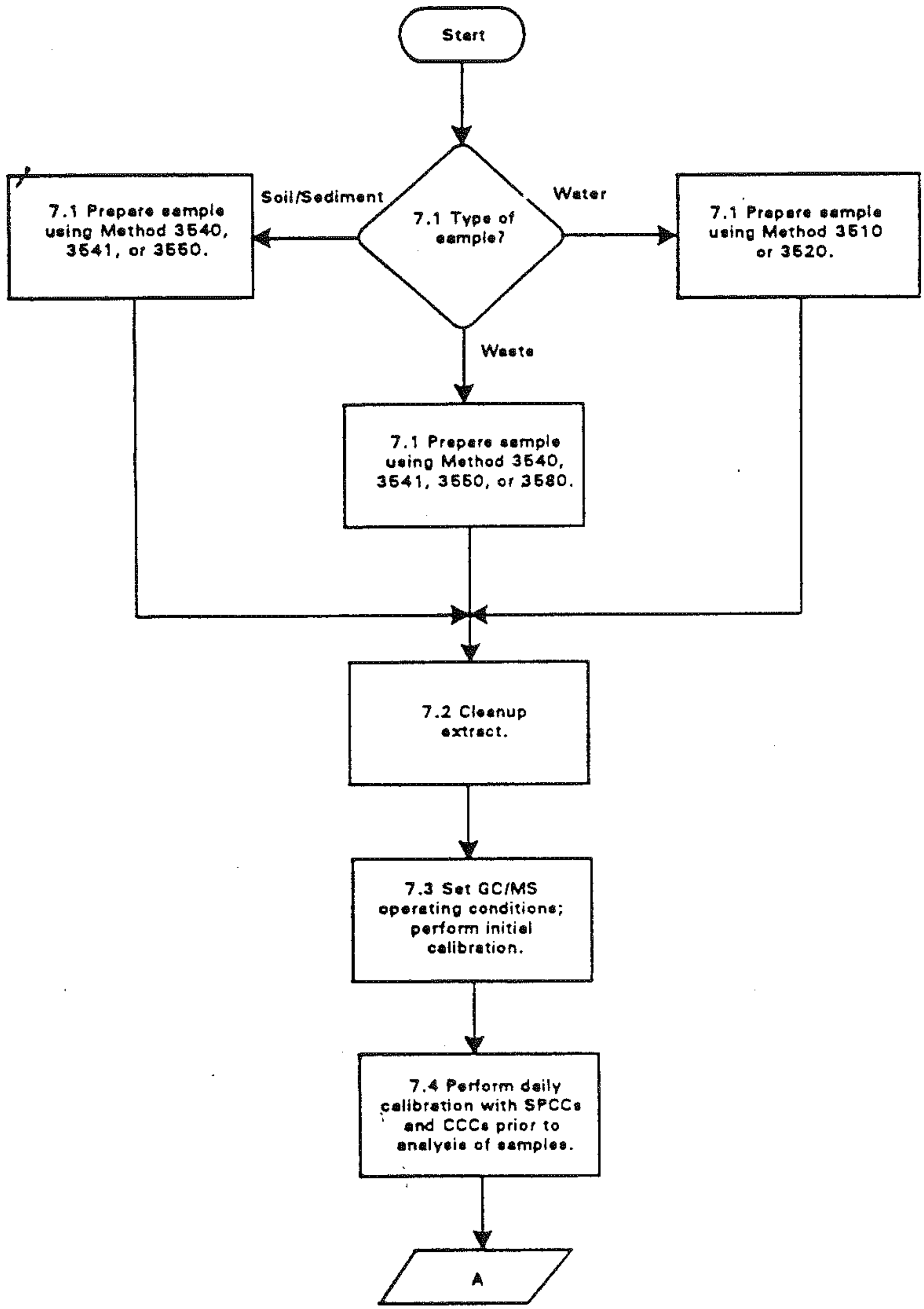
Compound	Amount Added (ug/L)	Recovery Ranges, %
Pyridine	100	25 - 125
1,4-Dichlorobenzene	100	25 - 125
2-Methylphenol	100	25 - 125
3 & 4-Methylphenol	100	25 - 125
Hexachloroethane	100	25 - 125
Nitrobenzene	100	25 - 125
Hexachlorobutadiene	100	25 - 125
2,4,6-Trichlorophenol	100	25 - 125
2,4,5-Trichlorophenol	100	25 - 125
2,4-Dinitrotoluene	100	25 - 125
Hexachlorobenzene	100	25 - 125
Pentachlorophenol	100	25 - 125

Table 7

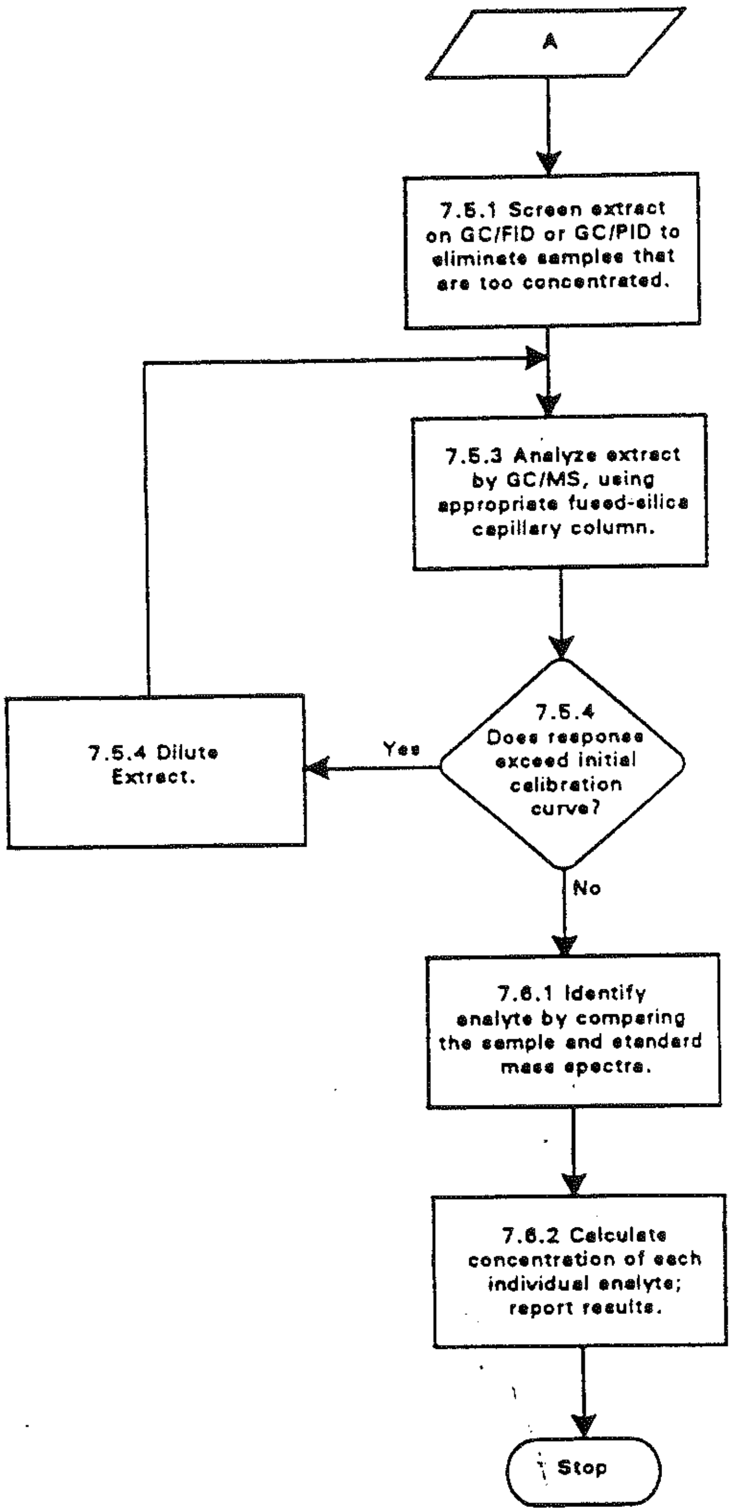
TCLP Lab Control Spike

Compound	Amount Added (ug/L)	Recovery Ranges, %
Pyridine	100	40 - 115
1,4-Dichlorobenzene	100	40 - 115
2-Methylphenol	100	40 - 115
3 & 4-Methylphenol	100	40 - 115
Hexachloroethane	100	40 - 115
Nitrobenzene	100	40 - 115
Hexachlorobutadiene	100	40 - 115
2,4,6-Trichlorophenol	100	40 - 115
2,4,5-Trichlorophenol	100	40 - 115
2,4-Dinitrotoluene	100	40 - 115
Hexachlorobenzene	100	40 - 115
Pentachlorophenol	100	40 - 115

METHOD 8270B
SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
(GC/MS) CAPILLARY COLUMN TECHNIQUE



METHOD 8270B
(Continued)



SOP No.: 13.0

Title: SOP for Method 8080A
Organochlorine Pesticides, PCBs and PCTs

1.0 SCOPE AND APPLICATION

1.1 Method 8080A is used to determine the concentration of various organochlorine pesticides, polychlorinated biphenyls (PCBs) and polychlorinated terphenyls (PCTs) in various matrices such as aqueous, solids, oils, products and wipes. Table 1 indicates compounds that may be determined by this method. The retention times for the pesticide compounds are also listed in Table 1.

TABLE 1

Retention Time Table

Target Compounds	Primary Column	Confirmation Column
alpha-BHC	5.90	8.77
gamma-BHC (Lindane)	6.88	11.00
Heptachlor	9.81	12.22
Aldrin	11.79	14.15
beta-BHC	6.72	17.09
delta-BHC	7.76	18.05
Heptachlor Epoxide	14.85	18.59
Endosulfan I	17.08	19.99
4,4'-DDE	18.60	21.86
Dieldrin	18.43	22.41
Endrin	19.57	23.93
Endosulfan II	20.18	28.73
4,4'-DDD	21.05	28.95
4,4'-DDT	23.70	29.86
Endrin Aldehyde	21.42	31.04
Endosulfan Sulfate	23.11	32.30
Methoxychlor	29.30	32.41
Endrin Ketone	26.96	33.36

	Rtx-5	Rtx-1701
Aroclor 1016	1. 6.52	1. 8.19
	2. 8.76	2. 10.15
	3. 10.08	3. 11.64
	4. 10.63	4. 13.11
	5. 12.15	5. 14.20
Aroclor 1260	1. 24.22	1. 25.24
	2. 27.05	2. 27.42
	3. 29.17	3. 30.07
	4. 30.67	4. 31.61
	5. 31.77	5. 32.57
Aroclor 1221	1. 5.66	1. 6.82
	2. 5.94	2. 7.42
	3. 6.11	3. 7.64
Aroclor 1232	1. 6.08	1. 7.64
	2. 8.21	2. 9.50
	3. 9.45	3. 12.27
	4. 9.98	4. 16.74
	5. 17.06	5. 17.28
Aroclor 1242	1. 6.07	1. 7.60
	2. 8.19	2. 9.45
	3. 9.43	3. 12.21
	4. 9.95	4. 13.24
	5. 17.04	5. 16.69
Aroclor 1248	1. 9.13	1. 9.13
	2. 12.41	2. 11.78
	3. 15.47	3. 16.31
	4. 15.71	4. 16.88
	5. 19.00	5. 22.48
Aroclor 1254	1. 16.15	1. 18.91
	2. 17.48	2. 19.96
	3. 18.83	3. 23.03
	4. 19.37	4. 25.01
	5. 24.65	5. 29.46
Aroclor 5432	1. 13.57	1. 16.00
	2. 14.75	2. 16.22
	3. 15.09	3. 17.64
	4. 16.15	4. 19.02
	5. 16.81	5. 19.37

	Rtx-5	Rtx-1701
Aroclor 5460	1. 21.77	1. 24.75
	2. 22.67	2. 25.12
	3. 23.21	3. 27.05
	4. 23.31	4. 27.32
	5. 24.33	5. 27.71
Chlordane	1. 9.27	1. 11.75
	2. 10.24	2. 12.82
	3. 14.87	3. 20.29
	4. 17.32	4. 21.14
	5. 21.57	5. 23.30
Toxaphene	1. 20.16	1. 29.80
	2. 22.53	2. 31.00
	3. 24.30	3. 31.38
	4. 25.01	4. 32.08
	5. 27.52	5. 32.34
Dibutylchlorendate (Sur)	30.86	32.69
Decachlorobiphenyl (Sur)	36.54	38.30

Additional compounds may be determined by this method. These compounds are suggested by Method 8081 and/or listed under Appendix IX compound list. Table 2 indicates compounds that can be analyzed by this method.

Table 2

Compound Name	CAS Registry No.
Chlorobenzilate	510-15-6
DBCP	96-12-8
Diallate	2303-16-4
Isodrin	465-73-6
Kepone	143-50-0
Alachlor	15972-60-8
Chorothalonil	1897-45-6
DCPA	1861-32-1
Mirex	2385-85-5
Propachlor	1918-16-17
Trans-Nonachlor	39765-80-5
Trifluralin	1582-09-8

2.0 SUMMARY OF METHOD

2.1 Method 8080A provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides,

polychlorinated biphenyls and terphenyls. Prior to the use of this method, appropriate sample extraction techniques must be used.

3.0 INTERFERENCES

3.1 Interferences by pthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large-eluting peaks, especially in the 15% and 50% fraction from cleanups. Interferences from pthalates can best be minimized by avoiding contact with any plastic materials.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph

Hewlett Packard GC Systems 5890 equipped with autosampler is used. Nelson or HP EnviroQuant software systems for data recording and processing is interfaced with the GC system.

4.2 Columns

4.2.1 Dual column connected with a "Y" connector to a single injection port is used. In this mode, material injected is split between the columns and detected by 2 separate ECD detectors.

4.2.2 Column 1: 30 meter, 0.53 I.D., 0.5 micron film thickness, Restek RTX-1701, fused silica column is used.

4.2.3 Column 2: 30 meter, 0.53 I.D., 0.5 micron film thickness, Restek RTX-5, fused silica column is used.

4.2.4 5 meter guard column (inert) is used at the "Y" connector.

4.3 GC Condition

4.3.1 The following GC parameters are implemented when Pest/PCBs are analyzed:

- Injection port temperature 265^{oC}
- Detectors temperature 300^{oC}
- A tri-ramp temperature program is used

1st Ramp:	
Initial temperature	$150^{o}C$
Initial time	0.5 min
Rate	$8^{o}C$/min
Final temperature	$180^{o}C$
Final time	10 min
2nd Ramp:	
Initial temperature	$180^{o}C$
Rate	$8^{o}C$/min
Final temperature	$210^{o}C$
Final time	10 min
3rd Ramp:	
Initial temperature	$210^{o}C$
Rate	15^{o}/min
Final temperature	$270^{o}C$
Final time	8 min

- Equilibrium time 0.75 min
- Septum purge on at 0.75 min at about 2ml/min
- Attenuation 0
- Signal rages 0
- Splitless purge 50ml/min
- Makeup gas 80ml/min

4.3.2 The following GC parameters are implemented when PCTs are analyzed:

Injector Temp	$280^{o}C$
Detector Temp	$300^{o}C$
Initial Temp	$150^{o}C$
Initial Time	0.5 min.
Ramp Rate	6^{o}/min.
Final Temp	$275^{o}C$
Final Time	15 min.

The Electronic Pressure Controller should be programmed as follows:

Initial Pressure Time	20min.
Initial Pressure	8 PSI
Rate	99 PSI
Final Pressure	25 PSI
Final Time	13min.

4.4 Gases

4.4.1 Helium ultrapure grade is used as a gas carrier at about 5ml per min at 50^{o} measured at the column end.

4.4.2 Make up gas is Argon/Methane (5% methane) and the flow rate is about 80 $\pm$ 5ml per min for each detector.

5.0 CALIBRATION

5.1 Calibration standards are prepared at five concentration levels through dilution of the stock standards with hexane (refer to standard logbook). Five ul of each level is injected. Concentrations of the compounds are listed on Table 3.

TABLE 3

	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)
4,4'-DDD	10	25	50	75	100
4,4'-DDE	10	25	50	75	100
4,4'-DDT	10	25	50	75	100
Aldrin	10	25	50	75	100
alpha-BHC	10	25	50	75	100
beta-BHC	10	25	50	75	100
Chlordane	100	250	500	1000	2000
Decachlorobiphenyl (PCB Surr)	25	62.5	125	187.5	250
delta-BHC	10	25	50	75	100
Dibutylchlorendate (Surrogate)	10	25	50	75	100
Dieldrin	10	25	50	75	100
Endosulfan I	10	25	50	75	100
Endosulfan II	10	25	50	75	100
Endosulfan Sulfate	10	25	50	75	100
Endrin	10	25	50	75	100
Endrin aldehyde	10	25	50	75	100
Endrin ketone	10	25	50	75	100
gamma-BHC (Lindane)	10	25	50	75	100
Heptachlor	10	25	50	75	100
Heptachlor epoxide	10	25	50	75	100
Methoxychlor	10	25	50	75	100
Toxaphene	100	250	500	1000	2000
AR1016	100	250	500	75	1000
AR1221	100	250	500	750	1000
AR1232	100	250	500	750	1000
AR1242	100	250	500	750	1000
AR1248	100	250	500	750	1000
AR1254	100	250	500	750	1000
AR1260	200	500	1000	1500	2000
AR5432	250	500	1000	2000	4000
AR5460	250	500	1000	2000	4000

5.2 Surrogate standard Decachlorobiphenyl is used in PCB analyses. It is calibrated at levels indicated on Table 3.

6.0 GC ANALYSIS

6.1 Retention time windows

6.1.1 Make 3 injections of all single component standard mixtures and multipeaks throughout the course of a 72-hour period. Calculate standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the cluster and calculate the standard deviation of the three retention times for that peak.

6.1.1.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define retention time window. For multipeak products, primarily combination of chromatography pattern and retention times are used.

6.1.1.2 In those cases where the standard deviation for a particular standard is zero, substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

6.1.1.3 When a new GC column is installed retention time window must be established. Typical retention times for 8080A target analytes under the parameters listed in Section 6.2 is provided on Table 1.

6.2 Degradation of DDT and Endrin

6.2.1 Check for degradation problems by injecting a mid-level standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). Degradation must be less than 20% before any sample analyzed.

$$\text{\% Breakdown for Endrin} = \frac{\text{Total DDT degradation peak area (DDE + DDD)} \times 100}{\text{Total DDT peak area (DDT + DDE + DDD)}}$$

$$\text{\% Breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area (endrin aldehyde+endrin ketone)} \times 100}{\text{Total Endrin peak area (endrin+endrin ketone+endrin aldehyde)}}$$

6.3 Calibration

6.3.1 Five level calibration is initially analyzed. Percent RSD (relative standard deviation) must be below 20% for all standards except surrogates and any 2 analytes which have % RSDs more than 20 but less than 30 percent. Same procedure must be applied for multiple peak compounds such as Toxaphene, PCBs and PCTs.

6.3.2 Continuing calibration is analyzed at the beginning of each shift. Percent difference should be kept at less than 15% for all compounds except for surrogates and any two analytes which have % RSDs more than 15 but less than 25 percent. A continuing (mid-level) calibration standard must also be injected between every 10 injections of samples and/or QC and at the end of every 12 hours whichever is more frequent.

6.3.3 Calibration sequence consists of initial or continuing pesticide injections followed by mid-level AR1660 (combined AR1016 and AR1260), mid-level Toxaphene and Chlordane. Other Aroclors are injected at mid-level initially. Reinjection of all Aroclors is necessary when retention time and/or sensitivity shifts are experienced. Experience of the chromatographer is an influential factor in determination of instrument drift and the necessity of injecting the entire Aroclor standards. Mid-sequence and closing standards include mid-level pesticide standard. Mid-sequence and closing multiple peak standard compounds are injected only when these analytes are exclusively required.

6.4 Sample Analysis

6.4.1 When all degradation and calibration requirements are met sample analysis may begin. After each batch of 10 runs degradation and linearity should be checked before any more samples analyzed.

6.4.2 Dilution must be made if the response exceed the linear range of the compounds.

6.4.3 Peak identification is based on detection on both columns. A daily retention time window is established for each analyte from section 5.1 as the midpoint of the window for that day. The daily retention time window equals the midpoint $\pm$ 3 times the standard deviation determined in section 5.1.

6.4.4 GCMS Confirmation is implemented if the concentration permits.

6.4.5 Wipe samples are treated like a solid sample and results are reported as ug per wipe. All QC parameters used for soil samples are applicable to wipes except for MS/MSD analysis. An actual MS/MSD analysis is impractical since only one wipe is sampled at a location and it can not be splitted.

6.5 PCBs

Initially 5 levels of standards for each Aroclor are analyzed and calibration curves are established. When PCBs analysis is required, a continuing calibration is analyzed for Ar-1660. If PCBs are detected in the sample, patterns are compared with initial standards and corresponding PCBs are analyzed for fingerprint match and retention time comparison. Calculation is based on average area or peak height quantification of 5 representative peaks. When interferences are present, those peaks with less interferences may be chosen for quantification. Also fewer peaks (minimum of 3) may be used for quantification if there are considerable interferences. Surrogate Decachlorobiphenyl (DCB) is used when only PCB analysis is required. DCB peak elutes past all PCB isomers and does not break down with acid cleanup.

6.6 PCTs

Initially 5 levels of standards containing only AR5432 and AR5460 are analyzed and calibration curves for each target analyte is established. Mid-level continuing calibrations are analyzed during the sequence run when PCTs are required. If PCTs are detected in the sample, patterns and retention times are compared with the calibration standard. Calculation is based on average area or peak height of 5 representative peaks. When interferences are present, those peaks with less interferences may be chosen for quantification. Also fewer peaks (minimum of 3) may be used for quantification if there are considerable interferences. Surrogate Decachlorobiphenyl (DCB) is used for quality control monitoring. Acid clean up can be performed if matrix effects are observed.

6.7 Toxaphene and Chlordane

Approach similar to 6.5

6.8 Low Concentration Method

This method is applicable to soil and water samples containing low level contaiminants with minimal matrix interferences. To achieve low detection limits, the final volumes of sample extracts are brought to 2.0 ml. Concentrations of surrogate adn matrix spike standards should be adjusted before extraction in order to produce levels comparable to low level procedure. Quality control and recovery ranges are not expected to be affected by final volume reduction and low level quality control criteria should be applicable to this modified method.

6.9 Calculation

6.9.1 All quantifications are based on external standard calculations.

6.9.1.1 Calculation for calibration factor

$$\text{Calibration factor} = \frac{\text{Total Area of Peak*}}{\text{Mass injected (nonograms)}}$$

* for multipeak analytes use total areas of all designated peaks for quantitation

6.9.1.2 Percent Difference

$$\text{Percent difference} = \frac{R_1 - R_2}{R_1} \text{ X } 100$$

R_1 = Calibration factor from first analysis
R_2 = Calibration factor from succeeding analyses

6.9.1.3 The concentration of each analyte in the sample may be determined by calculating the amount of standard injected from the peak response, using the calibration curve or factor determined from 6.7.1.1.

Aqueous Concentration (ug/L) = $[(A_x)(A)(Vt)(D)]/[(As)(Vi)(Vs)]$

Solid Concentration (ug/kg) = $[(A_x)(D)(A)(V_t)]/[(As)(Ws)(Vi)]$

where:

A_x = Response for the analyte in the sample, (area or peak height
A =Amount of standard injected in ng
As =Response for the external standard
Vi =Volume of extract injected
D =Dilution factor, if any
Vt =Volume of total extract

Vs =Volume of sample extracted
Ws = Weight of sample extracted

For non-aqueous samples, the unit is 1g/kg and dry weight of sample is used for Ws.

7.0 QUALITY CONTROL

7.1 Required Instrument QC

7.1.1 It is required that the % RSD vary by <20% when 5 point calibration factors are compared. Surrogates and 2 analytes may have RSDs above 20 but less than 30 percent.

7.1.2 It is required that difference of daily response of a given analyte vary $\pm$ 15% when compared to initial responses. Surrogates and 2 analytes may have percent difference above 15 but less than 25.

7.1.3 All succeeding standards in an analysis sequence must fall within daily retention time window established by the first standard of the sequence.

7.2 Matrix Spikes

7.2.1 For each analytical batch of up to 20 samples MS and MSD must be analyzed. If less than twenty samples are analyzed per month, MS/MSD must be analyzed on per month basis. Percent recoveries and Relative Percent Difference (RPD) should be calculated as follows:

$$\text{Matrix Spike \% Recovery} = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added from Spiking Mix

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

D1 = First Sample Value
D2 = Second Sample Value

Tables 4 and 5 lists the matrix compounds, amounts added and recovery ranges for soil and water matrices. If samples are analyzed for PCBs only, then matrix spikes must be analyzed for AR1016 and AR1260. Concentrations of these Aroclors are listed on Tables 4 and 5.

7.3 Lab Control Sample (LCS)

7.3.1 A control check sample is extracted and analyzed at frequency similar to MS/MSD with each extracted batch. Calculated concentrations are compared with the amount added and results are used to monitor of extraction and analytical process. When PCB analysis is needed the blank spike should be spiked with AR1016 and 1260 at the same levels as matrix spikes.

Table 7 lists the LCS compounds used for soil and water matrices and their associated recovery ranges.

7.4 Blanks

7.4.1 Blank is extracted and analyzed with each analytical batch. Blanks must be contaminant free. Concentration of any confirmed peak should be less than CRQL. Gross contaminations must be investigated if they interfere with analyte peaks.

7.5 Surrogates

7.5.1 Percent recoveries for the surrogates are periodically (minimum of once a year) determined by plotting percent recoveries of surrogates measured in 20 consecutive blanks. Control limits for each surrogate compound is measured using the following formula:

Upper Control Limit (UCL) = $p + 3s$
Lower Control Limit (LCL) = $p - 3s$

where p is the mean recovery and s is the standard deviation. Table 6 lists the recoveries of surrogates for different matrices.

8.0 SAFETY

8.1 Safety glasses for eye protection, laboratory coasts for body protection, latex gloves for hand protection.

8.2 Due to the toxicity or carcinogenicity of each reagent, each chemical compound should be treated as a potential health hazard.

8.3 Material Safety Data Sheets (MSDS) can be found on the procurement bookshelves located in the company library.

8.4 Preparation of the standard should be handled under a hood.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition

Table 4

Aqueous Pesticide Matrix Spike/Matrix Spike Duplicate Recovery

Compound	Spike Added (ug/L)	QC Limits RPD	QC Limits REC.
gamma-BHC (Lindane)	0.20	15	56-123
Heptachlor	0.20	20	40-131
Aldrin	0.20	22	40-120
Dieldrin	0.50	18	52-126
Endrin	0.50	21	56-121
4,4'-DDT	0.50	27	38-127
AR1016	5.0	30	20-125
AR1260	10	30	20-125
AR5460	20	30	20-125

Table 5

Non-Aqueous Pesticide Matrix Spike/Matrix Spike Duplicate Recovery

Compound	Spike Added (ug/kg)	QC Limits RPD	QC Limits REC.
gamma-BHC (Lindane)	6.7	50	46-127
Heptachlor	6.7	31	35-130
Aldrin	6.7	43	34-132
Dieldrin	16.7	38	31-134
Endrin	16.7	45	42-139
4,4'-DDT	16.7	50	23-134

PCBs	Spike Added (ug)	QC Limits RPD	QC Limits REC.
AR1016	5.0	50	20-125
AR1260	10.0	50	20-125
AR5460	20.0	50	20-125

Table 6

Surrogate Recovery For Soil and Water

Surrogate Compound	Amount Added (ug)	Water % Recoveries	Soil % Recoveries
Dibutylchlorendate (DBC)	1.0	24 - 154	24 - 150
Decachlorobiphenyl (DCB)	2.5	30 - 150	30 - 150

Table 7

Water and Soil Lab Control Spike

Water

Compound	Spike Added (ug/L)	QC Limits Recovery Range
gamma-BHC (Lindane)	0.20	45 - 125
Heptachlor	0.20	45 - 125
Aldrin	0.20	45 - 125
Dieldrin	0.50	45 - 125
Endrin	0.50	45 - 125
4,4'-DDT	0.50	45 - 125
AR1016	5.0	45 - 125
AR1260	10.0	45 - 125
AR5460	20.0	45 - 125

Soil

Compound	Spike Added (ug/kg)	QC Limits Recovery Range
gamma-BHC (Lindane)	6.7	40 - 130
Heptachlor	6.7	40 - 130
Aldrin	6.7	40 - 130
Dieldrin	16.7	40 - 130
Endrin	16.7	40 - 130
4,4'-DDT	16.7	40 - 130

PCBs	Spike Added (ug)	QC Limits Recovery Range
AR1016	5.0	40 - 130
AR1260	10.0	40 - 130
AR5460	20.0	40 - 130

SOP No.: 11.62

Title: Trace ICP Quantitation of HSL Metals plus Boron, Molybdenum, Silicon, Strontium, Titanium, and Tin.

Scope: The method detailed in this procedure is for the analysis of water, TCLP and EP extracts, soils, sludges, sediments and other solid wastes digestates for Hazardous Substance List (HSL) Metals by Inductively Coupled Plasma (ICP) spectroscopy in accordance with USEPA method 6010A. The use of ionization buffers, internal standards, and special background correction techniques is specified.

1.0 PURPOSE

The purpose of this procedure is to describe the simultaneous analysis of metals on the USEPA Hazardous Substances List (Antimony, Arsenic, Lead, Selenium, Silver, Thallium, Sodium, Potassium, Aluminum, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Vanadium, and Zinc) plus Boron, Molybdenum, Silicon, Strontium, Titanium, and Tin at trace levels using a Thermo-Jarrell-Ash 61E Purged Trace Inductively Coupled Plasma Spectrometer and autosampler. Table 1 lists the elements and contract required detection limits. All samples are digested in accordance with SOP 11.35 or 11.36 prior to analysis. Filtered samples for dissolved metals analysis can be analyzed after either digestion or matrix matching. The digestate holding time is 180 days.

2.0 REFERENCES

TJA ICAP 61E Operator's Manual (p/n 134542-00)

SW846 method 6010A revision 1

3.0 EQUIPMENT AND SUPPLIES

A.
- 100mL volumetric flasks
- 200mL volumetric flasks
- 500mL volumetric flasks
- 1000mL volumetric flasks
- 100mL plastic storage bottles
- 250mL plastic storage bottles
- 500mL plastic storage bottles
- 20.0L Nalgene carboy
- 10.0L Nalgene carboy
- 1000mL graduated cylinder
- 200mL graduated cylinders
- 15mL disposable autosampler tubes
- 28mL disposable autosampler tubes
- Centrifuge tube holder
- Pipetters and Pipette Tips
  - 1.000mL Rainin
  - .100mL Eppendorf
- 5, 10, 20 mL class A volumetric pipets
- Pump windings and tee fittings
- Argon gas (cryogenic liquid source)
- Nitrogen gas (cryogenic liquid source) used for purging of spectrometer

B. Instrumentation

TJA 61E Purge Trace ICP with meinhard nebulizer, cyclonic spray chamber, horizontal torch, and AS-192 autosampler.

Simultaneous background correction technique is used for the analysis of lead and selenium to acheive lower instrumental detection limits comparable to graphite furnace.

An argon humidifier is used for extracts and samples containing high salts. A high-solids "Bergener" nebulizer can be used for the analysis soil digestates.

Yttrium Internal standard - Lithium ionization buffer is added on-line using a mixing tee and coil with a ratio of 1:4 (one part standard: four parts samples, resulting in a dilution factor of 5 for the internal standard, approximated 1 ppm is the final, "mixed-in" concentration.

4.0 REAGENTS

Deionized water ASTM type II or equivalent

Concentrated hydrochloric acid, trace metals grade

Concentrated nitric acid, trace metals grade

Flame Water - 5% hydrochloric acid, 1% nitric acid

Preparation of flame water:

Fill a 20.0L Nalgene carboy half full with type II water. Add 200 ml concentrated nitric acid and 1000ml concentrated hydrochloric acid underneath a hood to contain noxious gases. Dilute to twenty liters with type II water and mix thoroughly.

2% nitric acid

Preparation of 2% nitric acid:

Fill a 10.0L Nalgene carboy half full with type II water. Add 200 mL of concentrated nitric acid underneath a hood. Dilute to ten liters with type II water and mix thoroughly.

Standards - Metal plasma grade standards which are traceable to NBS standard reference materials; High Purity Standards brand or equivalent.

ICV, CCV and ICS quality control standards currently supplied by High Purity Standards. LCS quality control standard currently supplied by Environmental Resources Associates.

5ppm Arsenic Profile check solution

Preparation of As solution:

Pipet 2.5mL of 1000ppm Manganese stock solution into a 500mL volumetric flask. Dilute to volume with flame water. Transfer to a bottle labelled 5ppm As. Record the date of preparation, expiration date and preparers initials on the bottle label. Prepare Arsenic Profile solution every three months or when depleted, whichever is more frequent.

Preparation of 5ppm Y-1000ppm Lithium Internal standard-ionization buffer:

Pipet 50 mL of 10,000 ppm Lithium standard (HPS cat # 10M29-1 or 10M29-2) and 2.5 mL of 1000ppm Yttrium standard (HPS cat # 100067-1) into a 500 mL volumetric flask, bring up to volume with matrix matched water (5% HCl+1% HNO3 or 2% HNO3).

5.0 GENERAL PRECAUTIONS

AVOID CONTAMINATION of STOCK STANDARDS. Always pour out a small volume of standard stock solution into a new microbeaker before taking an aliquot. NEVER insert a pipet directly into the bottle. This also applies to quality control standards stock solutions (ICVA, IC1, etc.)

Check pipetters daily for leaks and for proper calibration.

Empty Drain vessel at the end of each day. Take waste to waste disposal area for proper treatment prior to shipment. Fill vessel up to 6 inches of tap water prior to replacing beneath instrument.

Clean up and neutralize all spills immediately to avoid corrosion damage to the instrument.

Purge the optics with nitrogen at all times. Leave the RF power unit on at all times. Never attempt repairs to the High voltage systems. Leave the instrument PM tubes and heater on at all times.

6.0 PROCEDURE

6.1 Preparation of Calibration Standards

6.1.1 To prepare calibration Standard 2 in flame water, add 2.0ml of QC-19 (HPS cat#QCS-19), 20.0 mL of standard 2, part B, 2.0 mL of 10000 ug/mL sodium and 2.0 mL of 5ppm silver with either pipetters or glass pipets to a 200mL volumetric flask which has been half filled with flame water (or 2% nitric). Dilute the flask to volume with flame water (or 2% nitric). Mix the solution thoroughly, and transfer it to a plastic bottle.

6.1.2 To prepare calibration standard 2 in 2% nitric acid, follow the same procedure as with Standard 2 in flame water substituting 2% nitric acid for flame water.

6.1.3 To prepare calibration Standard 3 in flame water, add 20.0 ml of the multi-element standard CLP-INF-I from High Purity Standard with a glass A volumetric pipets to a 200mL volumetric flask which has been half filled with flame water. Dilute the flask to volume with flame water, mix the solution thoroughly, and transfer to a plastic bottle. Document and label the standard as described above. This standard is also used as the CLP interference check standard, part A.

6.1.3b To prepare calibration Standard 3 in 2% nitric acid, follow the same procedure as with Standard 3 in flame water substituting 2% nitric acid for flame water.

Standard 3	Starting CONC	Volume Added	Final CONC.
Iron	2000 ug/ml	10.0(mix)	200000 ug/L
Aluminum	5000	10.0(mix)	500000 ug/L
Magnesium	5000	10.0(mix)	500000 ug/L
Calcium	5000	10.0(mix)	500000 ug/L

NOTE 1: These formulations subject to change without an update of SOP to suit various client requirements

NOTE 2: If the client requires multiple standards for each element, the standards above will be used as the high standard, with 1:10 and 1:100 dilutions used for medium and low standards. Alternatively, the low, middle, and high standard can be prepared from decimal dilutions of the CRDL stock solution with the non-CLP elements added separately.

6.1.4 Document the standard in the ICP Standards Logbook (figure 1). Label the standard solution bottle. The label should include the preparers initials, the date of preparation, the expiration date, and the page number on which the standard has been recorded in the log book. The expiration date of standard solutions is three months from the date of preparation or whenever one of the certified standards expires, whichever is first.

Preparation of standard 2, part B stock solution, final volume 200ml.

Element	Certified Std. Conc.	Volume Added	Calibration Std. Conc.
Barium	10000ug/ml	2.0	10 ug/ml
Boron	1000	2.0	10
Potassium	10000	2.0	100
Silicon	1000	2.0	10
Strontium	1000	2.0	10
Tin	1000	2.0	10

(final volume = 200ml)

	Element	Certified Std. Conc.(ug/ml)	Volume Added (ml)	Calibration Std. Conc. (ug/L)
QC19	Antimony	100ug/ml	2.0(mix)	1000
	Arsenic	100	2.0(mix)	1000
	Beryllium	100	2.0(mix)	1000
	Cadmium	100	2.0(mix)	1000
	Calcium	100	2.0(mix)	1000
	Chromium	100	2.0(mix)	1000
	Cobalt	100	2.0(mix)	1000
	Copper	100	2.0(mix)	1000
	Iron	100	2.0(mix)	1000
	Lead	100	2.0(mix)	1000
	Magnesium	100	2.0(mix)	1000
	Manganese	100	2.0(mix)	1000
	Molybdenum	100	2.0(mix)	1000
	Nickel	100	2.0(mix)	1000
	Selenium	100	2.0(mix)	1000
	Thallium	100	2.0(mix)	1000
	Titanium	100	2.0(mix)	1000
	Vanadium	100	2.0(mix)	1000
	Zinc	100	2.0(mix)	1000
MIXB	Barium	10ug/ml	20(mix)	1000 ug/L
	Boron	10	20(mix)	1000
	Potassium	100	20(mix)	10000
	Silicon	10	20(mix)	1000
	Strontium	10	20(mix)	1000
	Tin	10	20(mix)	1000
SINGLE	Sodium	10000ug/ml	2.0	100000
SINGLE	Silver	5 ug/ml	2.0	125

Standard 2 (final volume = 200ml)

6.2 QC Preparation

6.2.1 Preparation of Contract Required ICP Detection Limit (CRI) Stock Solution. This standard can be purchased from High Purity standards, Cat # CRDL.

Fill a 100.0mL volumetric flask halfway with flame water and add the following:

Element	Conc.(ppb)	Volume Std (mL)	Certified Stock Conc.
Be	1000	.1000	1000 ppm
Cd	1000	.1000	1000 ppm
Cr	2000	.2000	1000 ppm
Co	10.00	1.000	1000 ppm
Cu	5.000	.5000	1000 ppm
Mn	3.000	.3000	1000 ppm
Ni	8.000	.8000	1000 ppm
V	10.00	1.000	1000 ppm
Zn	4.000	.4000	1000 ppm

(Note: Fe, Al, Ba, Mg, Ca, need not be added.) Dilute to the mark with flame water and transfer to a storage bottle. Document the solution in the ICP Standards Log Book (figure 1). Label the bottle as ICP CRI Stock and record the preparation date, the expiration date, the preparers initials, and the page number on which the solution has been recorded in the log book on the label. Prepare fresh solution every three months or when one of the certified standards expires.

6.2.2 Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV):

Fill a 100mL volumetric flask halfway with flame water and add one mL of ICVP, part A and part B certified stock solution, 0.5 mL of 1000 ug/ml Tin, and 0.5 mL of 1000 ug/ml Strontium. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled ICV. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the ICV solution using 2% nitric acid instead of flame water. These solutions should be prepared fresh daily.

6.2.3 Interference Check Standard A (ICSA):

Fill a 100mL volumetric flask halfway with flame water and add 10mL of CLP-INF-I certified multi-element stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled ICSA. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the ICSA solution using 2% nitric acid instead of flame water. These solutions should be prepared fresh daily.

6.2.4 Interference Check Standard AB (ICSAB):

Fill a 100mL volumetric flask halfway with flame water and add 10mL of CLP-INF-I certified stock solution, and 0.100mL of CLP-INF-II-Revised (Cat# ANALCS-R) certified stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled ICSAB. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the ICSAB solution using 2% nitric acid instead of flame water.

6.2.5 Contract Required Detection Limit Standard for ICP (CRI): Fill a 100mL volumetric flask halfway with flame water and add 1 mL of CRI stock solution or 0.10 ml of High Purity Standard's CRDL certified multi-element stock stock standard. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labelled CRI. If undigested filtered samples or drinking water samples are to be analyzed, then prepare the CRI solution using 2% nitric acid instead of flame water. These solutions should be prepared fresh daily.

6.3 Preparation of 1:5 Serial Dilution (L)

Obtain the sample digestates for the case or SDG to be analyzed. Take the original sample digestate that corresponds to the sample designated for duplicate and matrix spike digestions for each SDG and matrix and prepare its serial dilution as follows:

Into a 15mL centrifuge tube labelled (L), pipet the following:

2mL of sample
8mL of flame water

If undigested filtered samples or drinking water samples are to be analyzed, then prepare the serial dilution using 2% nitric acid instead of flame water. Prepare the serial dilution immediately before analysis.

6.4 Tuning and Calibration of the ICP

6.4.1 Conduct a pre-start up inspection.

6.4.1.1 Argon and Nitrogen gas supply and drain vessel

Make sure there is an adequate supply of Argon. Check the float gauge in the liquid argon dewar which is located in the cylinder storage room. The argon line pressure regulator should be set at 60 psi and the nitrogen line pressure should be set at 30 psi.

Check the drain vessel beneath the ICP and empty it if full.

6.4.1.2 Torch box

Make sure all connections are secure and air tight, including the drain hose, nebulizer cap, argon lines.

6.4.1.3 Peristaltic pump

Install new flexible pump tubing every other day (the windings have three stops which allow for an extra day of use) or if the old one shows signs of flattening or stretching, and connect to the nebulizer with capillary tubing.

6.4.2 Daily Start Up

6.4.2.1 Load the operating software called Thermospec by using the windows icon under Thermospec window or by typing "STNRUN" at the C: drive prompt in DOS.

6.4.2.2 Ignite plasma. Under the menu heading SET UP, select CONTROL PANEL; then press F1 for Start Up followed by F9 for continue to begin the start up sequence which takes about 90 seconds.

6.4.2.3 Warm-up. Once the torch has been successfully lit, exit the start up submenu and go to the analysis menu. At the method prompt, enter "6010" and the peristaltic pump should begin turning and the levels adjusted to following:

Torch gas = HIGH
Auxilary gas = LOW
Nebulizer gas = 0.588 mL/min
Approximate RF Power (W) = 950
Pump rate (RPM) = 130

Fill the rinse water reservoir with the same matix as the samples. Fill the internal standard - ionization buffer reservoir.

6.4.3 Profile and prepare for sample analysis.

6.4.3.1 Place a 28ml autosampler cup filled with 5 ppm As onto the last position (#19) on the "L" rack of the autosampler. Under the analysis submenu, press F6 to move autosampler and begin profile sequence. Once the autosampler has moved it will wait 35 seconds to allow for adequate uptake and equilibration of the test solution.

6.4.3.2 Start the profile sequence. Press F3 and then F1 to start the profile. The procedure takes approximately 63 seconds and returns a peak profile of the Arsenic line at 189.042 x 2 nm (second order line).

6.4.3.3 Record the peak position and intensity in the daily maintenance logbook. The peak position should be within 0.3 units of the 0 position and the intensity should be around 6000 "counts". Print out the profile report and include it with the raw data to demonstrate that the spectrometer was correctly profiled. A drift greater than the specified tolerance could indicate a drastic barometric or thermal change since the last profile and warrants further investigation. (see trouble shooting.)

6.4.4 Prepare autosampler sequence.

Under Operation menu, select "Autosampler Setup". Load the default table name "trace" and enter the samples to be run under set 2. (maxinum 192). Enter a CCV and CCB every 10 samples and an ICSA, ICSAB, CRI check sample every 80 samples. Once finished, print out the table assignments by pressing F2.

6.4.5 Load autosampler with standards and samples according to the table printouts. A typical set-up should like like this:

(set 1) Load autosampler L rack with 28 mL cups

Position	Standard
5	std1-blank
4	std2
3	std3
2	std4
1	Linear range solution
6	ICV solution
7,8	ICB, CCB solution
9	(skipped)
10	ICSA solution
11	ICSAB solution
12	CRI solution
13,15,17	CCV solution (for long runs)
14,16,18	CCB solution

(set 2) Load autosampler (48 position racks):

Position	Name
1	PBW (+DATE OF DIGESTION)
2	LCSW (+DATE OF DIGESTION)
3	SAMPLE
4	DUPLICATE D
5	SPIKE S
6	SERIAL DILUTION L
7	SAMPLE2
8	SAMPLE3
9	SAMPLE4
10	SAMPLE5
(13) of L rack	CCV
(14) of L rack	CCB
11 .. 20	10 more samples
(13) of L rack	CCV
(14) of L rack	CCB
21 .. 30	10 more samples
(13) of L rack	CCV
(14) of L rack	CCB
31 .. 40	10

(15) of L rack	CCV2
(16) of L rack	CCB2
41 .. 48,	8 more samples
rack 2, 1 .. 2	2 more samples
(15) of L rack	CCV2
(16) of L rack	CCB2

(set 3) The final QC is entered in set #3 and begins with a CCV/CCB pair.

(6) of L rack	ICV
(7) of L rack	ICB
(10) of L rack	ICSA
(11) of L rack	ICSAB
(12) of L rack	CRI
(1) of L rack	CCV
(8) of L rack	CCB

NOTE 1: The autosampler assigns the positions of the samples and QC in the order in which they are entered. Modifying an existing run by inserting samples may change the assignments of the samples.

NOTE 2: In order to take multiple uptakes from the same QC cup, the identical name must be entered. This would not allow for the numbering of CCV1/CCB1, CCV2/CCB2, etc. or the suffix of "I" or "F" on ICSA, ICSAB, CRI check solution used in CLP type packages.

6.5 Sample Analysis

6.5.1 Initiate autosampler run. Under the Operation menu, select Analysis, enter the method "6010", press F9 for autosampler run; enter the desired autosampler table file ("trace" if using example from 5.4.4) and press F1, to start operation.

6.5.2 If the samples to be analyzed have been digested then all the calibration standards and quality control solutions used should be prepared using flame water. If the samples to be analyzed are undigested filtered samples or drinking water samples, then all the calibration standards and quality control standards used should be prepared using 2% nitric acid.

6.5.3 Record the analysis sequence, the instrument identification, the date, the analyst's name, the analyst's signature, the time of analysis initiation, and the work order numbers on the bench sheet (figure 3). Submit a copy of the bench sheet with the raw data.

6.6 Quality Control Requirements

6.6.1 LINEAR RANGE CHECK.

The linear range sample is run immediately after calibration when analyzing samples by method 6010. The linear range sample is the high standard solution that was used to calibrate the instrument. The linear range sample result should be within 5% of the true value. This definition of linear range is typically much lower than the actual linear range of photo-multiplier tubes. When measurements for any element exceed the control limits, the analysis is void for that element. The problem must be corrected and the samples reanalyzed and diluted, if necessary, to bring the measured concentration within the analytical linear range.

6.6.2 ICV/CCV

The ICV is run immediately after calibration when analyzing samples by CLP method, or immediately after the linear range sample when running samples by method 6010. The CCV is run after every ten samples or every two hours. The ICV and CCV must be within 10% of the true value. When measurements for any element exceed the control limits the analysis is void for that element. The problem must be corrected and the samples reanalyzed.

Acceptance Criteria
ICV

Element	Control Limits (ppb)	True Value (ppb)
Antimony	90 - 110	100
Arsenic	36 - 44	40
Lead	18 - 22	20
Selenium	9 - 11	10
Silver	45 - 55	50
Thallium	45 - 55	50
Aluminum	1800 - 2200	2000
Barium	1800 - 2200	2000
Beryllium	45 - 55	50
Cadmium	45 - 55	50
Calcium	9000 - 11000	10000
Chromium	180 - 220	200
Cobalt	450 - 550	500
Copper	225 - 275	250
Iron	1800 - 2200	2000
Magnesium	9000 - 11000	10000
Manganese	450 - 550	500
Nickel	450 - 550	500
Vanadium	450 - 550	500
Zinc	450 - 550	500
Potassium	9000 - 11000	10000
Sodium	9000 - 11000	10000
Molybdenum	450 - 550	500
Boron	450 - 550	500
Silicon	450 - 550	500
Strontium	450 - 550	500
Titanium	450 - 550	500
Tin	450 - 550	500

6.6.3 ICB/CCB

The ICB and CCB are blank solutions. The ICB must be run immediately after the ICV. A CCB must be run immediately after each CCV. The absolute value of the ICB and CCB measurements should be less than or equal to the EPA CRDL (ILM03.01). Otherwise, the analysis is void for that element. The problem must be corrected and the samples reanalyzed.

Element	CRDL (ppb)
Antimony	6
Arsenic	10
Lead	3
Selenium	5
Silver	10
Thallium	10
Aluminum	200
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Magnesium	5000
Manganese	15
Nickel	40
Vanadium	50
Zinc	20
Potassium	5000
Sodium	5000
Molybdenum	10
Boron	50
Silicon	200
Strontium	5
Titanium	50
Tin	40

6.6.4 ICSAB

The ICSA and ICSAB must be run at the beginning and end of each analysis run or at a minimum of twice per eight hour shift. ICSAB must be run immediately following ICSA. ICSA contains interferents. ICSAB contains analytes plus interferents. The ICSA and ICSAB measurements must be within 20% of the true values. If any element is outside this limit, then the analysis is void for that element. The problem must be corrected and the element should be reanalyzed.

Acceptance Criteria
ICSAB

Element	Control Limits (ppb)	True Value (ppb)
Antimony	480 - 720	600
Arsenic	80 - 120	100
Lead	40 - 60	50
Selenium	40 - 60	50
Silver	160 - 240	200
Thallium	80 - 120	100
Aluminum	400000 - 600000	500000
Barium	400 - 600	500
Beryllium	400 - 600	500
Cadmium	800 - 1200	1000
Calcium	400000 - 600000	500000
Chromium	400 - 600	500
Cobalt	400 - 600	500
Copper	00 - 600	500
Iron	160000 - 240000	200000
Magnesium	400000 - 600000	500000
Manganese	400 - 600	500
Nickel	400 - 600	1000
Vanadium	400 - 600	500
Zinc	800 - 1200	1000
Potassium	NR	
Sodium	NR	
Molybdenum	400 - 600	500
Boron	400 - 600	500
Silicon	400 - 600	500
Strontium	400 - 600	500
Titanium	400 - 600	500
Tin	400 - 600	500

6.6.5 CRI

The CRI is to verify linearity near the CRDL (see table 1). The CRI is prepared at two times the concentration of the CRDL or approximately 3 - 5 times the IDL if a CRDL does not exit for a particular element. If samples are being run by method 6010, then the CRI must be run at least once during the analysis. Specific acceptance criteria currently do not exist in the current protocols but a range of +/- 25% or +/- CRDL (whichever is higher) will be used as rejection criteria.

6.6.6 PBW/PBS

The PBW and PBS are laboratory digested blanks. If any element concentration in the digested blank is above CRDL (see table 1), then all the samples associated with that blank which have concentrations greater than the CRDL and less than ten times the blank concentration must be redigested and reanalyzed for that element. If any element concentration in the digested blank is less than the negative of the CRDL, then all samples associated with that blank must be reanalyzed.

6.6.7 LCSW/LCSS

The LCSW and LCSS are digested control samples. The LCSW measurements must be within 20% of the true values. If any element concentration in the LCS is outside the control limits, then all the samples associated with that LCS must be redigested and reanalyzed.

Acceptance Criteria
LCSW

Element	Control Limits (ppb)	True Value (ppb)
Antimony	80 - 120	100
Arsenic	32 - 48	40
Lead	16 - 24	20
Selenium	8 - 12	10
Silver	40 - 60	50
Thallium	40 - 60	50
Potassium	8000 - 12000	10000
Sodium	8000 - 12000	10000
Aluminum	1600 - 2400	2000
Barium	400 - 600	500
Beryllium	80 - 120	100
Cadmium	400 - 600	500
Calcium	8000 - 12000	10000
Chromium	400 - 600	500
Cobalt	400 - 600	500
Copper	400 - 600	500
Iron	1600 - 2400	2000
Magnesium	8000 - 12000	10000
Manganese	400 - 600	500
Nickel	500 - 600	500
Vanadium	400 - 600	500
Zinc	400 - 600	500
Molybdenum	400 - 600	500
Boron	400 - 600	500
Silicon	400 - 600	500
Strontium	400 - 600	500
Titanium	400 - 600	500

Acceptance Criteria
LCSS

The manufacturer (ERA, Arvada CO) supplied control limits are used unless otherwise specified.

6.6.8 Duplicates

One duplicate must be analyzed for each matrix type in each group of samples. If an element concentration is greater than or equal to five times the CRDL, then the % RPD should be 20%.

$$\%RPD = \frac{\text{sample - dup}}{\frac{\text{sample + dup}}{2}} \times 100$$

6.6.9 Matrix Spike and Post Digestion Spike Samples

The spike sample analysis is designed to provide information regarding the digestion and methodology used for analysis. One spike is prepared for each matrix type in each group of samples. If the spike recovery for an element is less than 25% of the true value, and if the sample concentration corresponding to the spiked sample is less than four times the spike added, then a post digestion spiked sample must be run. The post digestion spike must be twice the sample concentration or twice the CRDL, whichever is greater. For purposes of calculating the % spike recovery, sample results less than the instrument detection limit (IDL), should be assumed to be zero.

Element	Aqueous (ppb)	Solid (ppb)
Antimony	100	100
Arsenic	40	40
Lead	20	20
Selenium	10	10
Silver	50	50
Thallium	50	50
Aluminum	2000	not required
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	not required	not required
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	not required
Magnesium	not required	not required
Manganese	500	500
Nickel	500	500
Vanadium	500	500
Zinc	500	500
Potassium	10000	10000
Sodium	10000	10000
Molybdenum	500	500
Boron	500	500
Silicon	500	500
Strontium	500	500
Titanium	500	500
Tin	500	500

6.6.10 Serial Dilution

One serial dilution is prepared for one sample of each matrix type in each group of samples. If the element concentration is fifty times the IDL or greater, then the % difference between the serial dilution and the sample should be 10%.

$$\% \text{ Difference} = \frac{\text{sample} - \text{dilution}}{\text{sample}} \times 100$$

6.7 Instrument Shut Down

6.7.1. Aspirate flame water for several minutes, followed by DI water, followed by 2% Triton-X 100, followed by DI water, to clean nebulizer tips and spray chamber.

6.7.2. Under Setup menu, select F7 (shutdown). This shuts off the torch and pump windings, goes through a cool down period of 90 seconds before shuting off the water recirculator and gas flows.

6.7.3. After the peristaltic pump stops, disengage the top two cartridges, leaving the tension setting untouched. The bottom cartridge supplies tension to the rinse reservoir and should be kept on to prevent back flowing of the rinse water.

6.7.4. Leave the circuit breaker on the RF power unit behind the instrument on at all times.

6.7.5. Leave the nitrogen purge gas on at all times.

6.8 Trouble shooting and corrective action

6.8.1 Problem: Stable plasma will not start.

Action: Make sure the pump tubing is stalled and that there are no leaks in the tubing or spray chamber. Make sure the drain line is submerged under 6 inches of water in the drain waste vessel.

6.8.2 Problem: Profile peak position greater than 0.3 units from zero position.

Action: ICP may not have reached purge or thermal equilibrium. Check the nitrogen purge gas flow, replace nitrogen dewar if empty or low pressure prevents sufficient purging. If purge is sufficient, try re-profiling and recalculate spectrum shifter position. Set new vernier position and verify profile. Record new vernier position in daily maintenance log.

6.8.3 Problem: ICV fails for an element.

Action: (a) The instrument will need to be recalibrated. (b) The profile may have drifted beyond 0.3 units from zero position. (c) The sample introduction system may have deteriorated since calibration indicating the nebulizer tip, pump windings, etc. may need cleaning or replacement. (d) The internal standard may have run out. (e) the ICV solution or sample introduction system may have been contaminated, perform additional rinse, refill ICV/CCV, and rerun to verify. (f) The calibration standards may need to be remade.

6.8.4 Problem: ICB fails for an element.

Action: (a) The instrument will need to be recalibrated. (b) The profile may have drifted beyond 0.3 units from zero position. (c) The sample introduction system may have deteriorated since calibration indicating the nebulizer tip, pump windings, etc. may need cleaning or replacement. (d) The internal standard may have run out. (e) the ICB solution or sample introduction system may have been contaminated, perform additional rinse, refill ICB/CCB, and rerun to verify. (f) The calibration standards may need to be remade.

6.8.5 Problem: ICSA or ICSAB fails for an element.

Action: (a) The spectrum shifter may need to be reprofiled, (b) the Interelement correction files may need to be changed or (c) new background points may need to be selected and new IEC performed.

7.0 SAFETY

7.1 Equipment

1. Lab coat
2. Safety glasses
3. Gloves

7.2 Potential hazards

7.2.1 All samples and solutions are in 5% HCl and may contain high concentrations of metals a well. Safety glasses should be worn to protect the eyes from acid splashes. Gloves and lab coats should be worn to protect the hands and skin from spills or splatter. If any solution is spilled on the skin, wash the area immediately with plenty of water and notify a supervisor. If any solution is splashed in the eyes, rinse immediately and thoroughly in an eyewash basin and contact a supervisor immediately.

7.2.2 The ICP uses high voltage electricity and generates an RF field, so there is a potential risk of electrocution if shielding is circumvented. The TJA ICP has numerous safety interlocks to shut off power to the RF coils if there is a break in the shielding around the coils, if the supply of cooling water is lost, or if there is a loss of argon pressure.

8.0 DISPOSAL REQUIREMENTS

8.1 After analysis sample digestates must be held for six months, after which they are disposed of in accordance with the Hazardous Waste Disposal Procedure.

8.2 All other non hazardous solutions may be washed down the drain with copious amounts of water.

9.0 REPORTING REQUIREMENTS

9.1 The case number, date, instrument ID, analyst's initials, and page number or source of all standard and quality control solutions must be recorded on the first page of raw data.

9.2 The ICP run log (figure 2) must be filled out for each day's operations. The method, date & time of start and end of each run, standard sequence and sources, QC sequence and sources, and sequence of samples analyzed and date for preparaton batch. In addition, each run must be recorded according to work orders, fraction numbers, corresponding multi-pro file name, elements completed, and analyst's initials.

9.3 If any maintenance is performed, routine or non-routine, the Maintenance log for the affected ICP shall be filled out (figure 4). This shall accompany all field service reports.

9.4 Record all solutions made in the ICP Calibration Standards logbook (figure 1).

Table 1
Contract Required Detection Limit

Element	CRDL (µg/L)	
Antimony	6	F
Arsenic	10	F
Lead	3	F
Selenium	5	F
Silver	10	F
Thallium	10	F
Aluminum	200	
Barium	200	
Beryllium	5	
Cadmium	5	
Calcium	5000	
Chromium	10	
Cobalt	50	
Copper	25	
Iron	100	
Magnesium	5000	
Manganese	15	
Nickel	40	
Vanadium	50	
Zinc	20	
Potassium	5000	A
Sodium	5000	A
Molybdenum	10	*
Boron	50	*
Silicon	200	*
Strontium	5	*
Titanium	50	*
Tin	40	*

A - May also be performed by FLAA
F - Element traditionally performed on GFAA
* - Element not on Hazardous Substances List.

FLAA = Flame Atomic Absorption
GFAA = Graphite Furnace Atomic Absorption

Figure 1
ICP CALIBRATION LOG BOOK

Figure 1

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GP ENVIRONMENTAL SERVICES ***** METALS WORKING STANDARDS LOGBOOK

Document Control No.: GP163 Page No.: 205

Type: ______ Date Prepared: ______ Initials: ______

Matrix: ______ Date of Expiration: ______ Supervisor: ______

Element	A Starting Conc(ppm)	B Volume Added(ml)	C Final Volume(ml)	AxB/C Final Conc(ppm)	Std Source page # or (GP ID no)	Date of Expire
Zinc					Zn	
Beryllium					Be	
Cadmium					Cd	
Manganese					Mn	
Barium					Ba	
Cobalt					Co	
Copper					Cu	
Vanadium					V	
Chromium					Cr	
Nickel					Ni	
Iron					Fe	
Aluminum					Al	
Magnesium					Mg	
Calcium					Ca	
Arsenic					As	
Selenium					Se	
Silver					Ag	
Lead					Pb	
Thallium						

Comments: ______

GP ENVIRONMENTAL SERVICES

Figure 2
ICP RUN LOG

Document Control No.:__________ Page_____

GP ENVIRONMENTAL SERVICES TRACE ICP RUN LOG

Instrument ID Number: Trace Method :______________ File:_____________

Start Date.:_______________ End Date:_________________ MP FILENAME:________

GPWorkorder	Clientcode	Type	Matrix	Prepdate	Comments:(Rush, Redigestion,etc)

AdditionalComments:____

Maintenance: Pump windings ______ Waste ________ Nitrogen Purge:_______

Aresenic Profile Peak Position:_____________ Intensity:__________

Traceability:

S1:__________________ ICV :_________________ Y INTERNAL STD:______________
S2:__________________ CCV :_________________ LITHIUM BUFFER:______________
S3:__________________ ICSA :_________________ Nebulizer ID :______________
S4:__________________ ICSAB:_________________
S5:__________________ CRI :_________________

Analyst:_____________________________ Reviewed: ______________________________

Figure 3
Bench Sheet

BENCH SHEET
SW6010

DATA FILE: W042296A | CASE: | SDG:
INSTRUMENT FILE: | INSTRUMENT: TRACE | ANALYZED: 04/22/96

SEQ	LAB ID	CLIENT ID	MATRIX	DILUTION	SIZE	VOLUME	%SOLIDS	ANALYZED	
1	STANDARD 1	S0	WATER	1.00	100.000	100.000		04/22/96	10:31:09
2	STANDARD 2	S1000	WATER	1.00	100.000	100.000		04/22/96	10:36:11
3	STANDARD 3	S3	WATER	1.00	100.000	100.000		04/22/96	10:40:10
4	STANDARD 4	S4	WATER	1.00	100.000	100.000		04/22/96	10:44:40
5	ZZZZZZ	ZZZZZZ	Water	1.00	100.000	100.000		04/22/96	10:44:50
6	STANDARD 5	S5	Water	1.00	100.000	100.000		04/22/96	10:54:12
7	ICV	ICV	WATER	1.00	100.000	100.000		04/22/96	10:56:49
8	ICB	ICB	WATER	1.00	100.000	100.000		04/22/96	11:01:51
9	ICSAI	ICSAI	WATER	1.00	100.000	100.000		04/22/96	11:06:53
10	ICSABI	ICSABI	WATER	1.00	100.000	100.000		04/22/96	11:11:54
11	CRII	CRII	WATER	1.00	100.000	100.000		04/22/96	11:16:56
	CCV	CCV1	Water	1.00	100.000	100.000		04/22/96	11:21:59
13	CCB	CCB1	Water	1.00	100.000	100.000		04/22/96	11:27:01
14	PBW4/20/96	PBW	WATER	1.00	100.000	100.000		04/22/96	11:32:02
15	LCSW4/20/96	LCSW	WATER	1.00	100.000	100.000		04/22/96	11:37:04
16	9604126-01H	T7-22-EFS-041996	WATER	1.00	100.000	100.000		04/22/96	11:42:05
17	9604126-01HD	T7-22-EFS-041996D	WATER	1.00	100.000	100.000		04/22/96	11:47:06
18	9604126-01HS	T7-22-EFS-041996S	WATER	1.00	100.000	100.000		04/22/96	11:52:07
19	9604126-01HL	T7-22-EFS-041996L	WATER	5.00	100.000	100.000		04/22/96	11:57:07
20	9604114-01C	GW-6	WATER	1.00	100.000	100.000		04/22/96	12:02:08
21	9604114-01CD	GW-6D	WATER	1.00	100.000	100.000		04/22/96	12:07:09
22	9604114-01CS	GW-6S	WATER	1.00	100.000	100.000		04/22/96	12:12:10
23	9604114-01CL	GW-6L	WATER	1.00	100.000	100.000		04/22/96	12:17:11
24	CCV	CCV2	Water	1.00	100.000	100.000		04/22/96	12:22:12
25	CCB	CCB2	Water	1.00	100.000	100.000		04/22/96	12:27:14
26	9604121-01A	MW	WATER	1.00	100.000	100.000		04/22/96	12:32:16
27	9604126-02A	T7-22-EFS-041996(FILTERED)	WATER	1.00	100.000	110.000		04/22/96	12:37:17
28	9604126-02ALD	T7-22-EFS-041996(FILTERED)LD	WATER	1.00	100.000	110.000		04/22/96	12:42:19
29	9604126-02AL	T7-22-EFS-041996(FILTERED)L	WATER	5.00	100.000	110.000		04/22/96	12:47:20
30	CCV	CCV	Water	1.00	100.000	100.000		04/22/96	12:52:23
31	CCB	CCB	Water	1.00	100.000	100.000		04/22/96	12:57:25
	ICSAF	ICSAF	Water	1.00	100.000	100.000		04/22/96	13:03:26
[illegible]	ICSABF	ICSABF	Water	1.00	100.000	100.000		04/22/96	13:07:27
34	CRIF	CRIF	Water	1.00	100.000	100.000		04/22/96	13:12:29
35	CCV	CCV	Water	1.00	100.000	100.000		04/22/96	13:17:31
36	CCB	CCB	Water	1.00	100.000	100.000		04/22/96	13:22:33

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Controlled Copy No. 6

Effective Date: October 1995
Version Number: 1.0
Initiated By:
Approved By:

SOP No.: 11.55

Title: Chloride - (Titrimetric, Mercuric Nitrate)

Scope: This Standard Operating Procedure describes the method for the determination of Chloride according to EPA Method 325.3

I. PURPOSE

This method explains the determination of chloride in soils, sediments, and water. The applicable range of this method is from 0.50 mg/L chloride.

Inorganic chloride is measured by titration. An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

II. REFERENCES

- U.S. EPA Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 325.3
- U.S. EPA Methods for Handling and Chemical Analysis of Sediment and Water Samples, 1981, p. 3-183.

III. SAMPLE HANDLING AND PRESERVATION

Analysis should be performed within 28 days of sampling. Until analysis, the sample should be preserved by refrigeration at 4°C.

IV. EQUIPMENT AND SUPPLIES

- 5 or 10 ml buret with 0.05 ml graduations
- Magnetic stir bar and stir plate

V. REAGENTS AND STANDARDS

- Stock mercuric nitrate titrant(0.141N):
  Dissolve 25 grams of $Hg(NO_3)_2\ H_2O$ in 800 ml of water acidified with 5.0 ml of conc. HNO_3. Dilute to 1 liter. Filter is necessary.

- Mercuric nitrate titrant (0.0141N):
  Dilute 100 ml of stock titrant to 1 liter

- Mixed indicator solution:
  Dissolve 0.5 grams crystalline diphenylcarbazone and 0.05 grams bromophenol blue powder in 75 ml of 95% ethanol. Dilute to 100 ml with ethanol and store in a dark bottle, refrigerated. Solution is good for 6 months.

- Nitric acid solution:
  Add 3.0 ml nitric acid to 997 ml of water

- Sodium hydroxide solution:
  Dissolve 10 grams of NaOH in water with mixing and dilute to 1 liter.

- Stock chloride solution, 1000 mg/L:
  This solution can be purchased with certificates of analysis.

VI. PROCEDURE

A. Standardization of Titrant

1. Titrate a standard chloride solution (25 mg/L) as described in B. below.

2. Calculate the concentration of the titrant by:

$$\text{Normality titrant, N} = \frac{(50\ \text{ml Cl-})\ (25\ \text{mg/L Cl-})}{(\text{X ml titrant})\ (35{,}450)}$$

B. A titrant blank should be analyzed before any samples, to establish the amout of titrant required to reach the endpoint color for blank water plus the reagents to be used with the samples.

C. Water Samples

1. Place 50 ml of sample, or a portion of sample diluted to 50 ml, in a flask. Add the stir bar and place flask on stir plate.

2. Add 5 - 10 drops of mixed indicator

3. If a blue-violet or red color appears, add nitric acid solution dropwise until the color changes to yellow.

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4. If a yellow or orange color forms when indicator is added, add NaOH solution dropwise until color changes to blue, then add nitric acid solution dropwise until color changes to yellow.

5. Add 1 ml excess nitric acid solution

6. Titrate with 0.0141 N titrant until a blue-violet color persists throughout the solution. Practice runs should be made to familiarize the analyst with the endpoint.

7. Samples requiring more than 10ml of titrant to reach the endpoint should be diluted.

D. Soil and Sediment Samples

1. Weigh a 0.5- to 1.0-g sample of the wet sediment. Transfer to a 100-ml Erlenmeyer flask.

2. Add 50 ml distilled water to the sample and boil for 15 minutes. Since the procedure is operationally defined, the heating time should be standard for all samples.

3. Transfer the sample to a centrifuge tube and centrifuge the slurry at 2,000 rpm for 5 to 10 minutes. Decant the liquid phase into a 100-ml volumetric flask.

4. Add 10 ml distilled water to the solids in the centrifuge tube and thoroughly mix the sample. Centrifuge for 5 to 10 minutes at 200 rpm. Decant the wash into the volumetric flask.

5. Repeat the washing procedure a second time and add the wash to the volumetric flask. Dilute the sample to volume with distilled water. Filter through a 0.45μ pore-size membrane filter.

6. Analyze the extract as a water sample.

E. Calculation

1. For water samples:

$$\text{mg Cl}^-/\text{L} = \frac{(A - B)N \times 35.450}{\text{ml of sample}}$$

Where:

A = ml titrant for sample
B = ml titrant for blank

N = normality of mercuric nitrate titrant

2. For soil and sediment samples, determine the chloride concentration of the sediment sample as follows:

Dry basis: $$\text{chloride, mg/kg} = \frac{(x)\ (y)\ (1{,}000)}{g\ (\%S)}$$

Where:

x = chloride concentration in sample, mg/L

y = sample volume, liter

g = wet weight of sediment sample, g

%S = percent solids in sediment (as decimal fraction)

VII. QUALITY CONTROL

A. At the beginning of an analytical run, the initial calibration must be verified by an EPA Control Sample. The percent recovered (%R) is calculated as follows:

$$\frac{\text{Found value}}{\text{True value}} = \%R \text{ must be within the specified 95\% C.I.}$$

A continuing calibration verification must be run after every ten samples or at the end of a case, and calculated as above. The initial calibration must be rerun if the first value fails. If any continuing calibration fails, those samples affected must be rerun.
If no control limits are supplied for the ICV/CCV sample, recovery limits of 85-115% will be used.

B. Duplicate sample analysis must be performed for every 20 samples of the same matrix. The difference between the two values is defined as Relative Percent Difference and is calculated as follows:

$$RPD = \frac{(\text{Sample-Duplicate})^2}{\text{Sample+Duplicate}} \times 100 \quad \text{must be} \leq \pm\ 15\%$$

C. Spiked sample analysis must be performed for every 20 samples of the same matrix. Samples should be spiked with an amount 2-5 times the method detection limit. If sample results are high (sample requires dilution), the matrix spike should be at least half the concentration of the sample. Spike recovery must be 80-120%. Percent recovered is calculated as follows:

$$\frac{\text{Spiked Sample - Sample}}{\text{Spike Added}} \times 100 = \%R$$

D. Along with the initial calibration verification sample, an initial calibration blank (ICB) must be analyzed, with results below the detection limit, before the analysis of samples. Similarly, continuing blanks (CCB's) will be analyzed along with the CCV's after every ten samples, with the same result limit.

VIII. REPORTING REQUIREMENTS

For each case of samples analyzed, the following must be submitted:

- The appropriate final report
- A copy of the raw data from analyte's notebook.

IX. SAFETY

Wear safety glasses, lab coat and gloves at all times. Wash hands thoroughly after removing gloves.
Use caution when handling strong acids and bases.

ETC/EDISON IS NOW PACE/NJ

TITLE: The Analysis of Environmental Sample Extracts for Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans Using Gas Chromatography/Mass Spectrometry by SW-846 Method 8280	Doc.#EX420301
Approval: Lab Manager	Revision #1
Review: QA Manager	Effective Date 04/12/93

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical waste extracts using computerized high resolution Gas Chromatography/Mass Spectrometry.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is specific for the following A-Types:

1 AP9/PCDX, 2 AP9/PCDX, 1 PCDX/8280, 2 PCDX/8280, 3 PCDX/8280, 4 PCDX/8280, ISO/2378.

2.0 SUMMARY OF METHOD

2.1 Environmental samples are extracted and prepared for analysis following the procedures outlined in ETC SOP EX411900. The GC/MS instrument is calibrated for mass assignment, abundance, instrument response, and chromatographic retention time using PCDD and PCDF reference standard solutions (Cl_4-Cl_8) which have been internal standardized with ^{13}C labeled analogs of several PCDD and PCDF reference compounds. The prepared sample extracts (which have been internal standardized prior to extraction) are also analyzed by GC/MS. PCDDs and PCDFs detected in the extracts which meet specific criteria are qualitatively and quantitatively identified using chromatographic relative retention time information, mass abundance information, and calibration response factors.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic date. All these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents help to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is know to resolve all of the isomers.

.0 SAFETY

4.1 Human Toxicology

4.1.1 The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 part-per-trillion, but the solubility in various organic solvents ranges from 0.001 percent to 0.14 percent.

4.1.2 On the basis of the available toxicological and physical property data and TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

4.2 Safety Equipment

4.2.1 Safe Lab Practice

PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling any contaminated environmental sample. Well-ventilated, controlled-access laboratories are required, and laboratory personnel entering these laboratories should wear appropriate safety clothing.

4.2.2 Protective Clothing

Eye protection equipment must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, when handling samples.

4.2.3 Other Lab Safeguards

Benches and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. The effluent from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

4.3 Disposal

All laboratory ware, safety clothing, and other items potentially contaminated with PCDD, PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approval steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration of EPA-approved facilities.

5.0 APPARATUS AND MATERIALS

5.1 Gas chromatograph/mass spectrometer data system.

5.1.1 Gas Chromatograph: An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns and gases.

5.1.2 Fused silica capillary columns.

5.1.2.1 Capillary columns which provide separation of 2,3,7,8 TCDD from all other TCDD isomers equivalent to that specified in Section 6.3 must be used; this separation must be demonstrated and documented using the performance test mixture described in Section

6.3. The following columns have been demonstrated to meet the separation criteria specified in Section 6.3. DB-5 is employed by ETC as the column of choice for dioxin analysis unless special applications explicitly require the use of an alternate column.

(a) DB-5 (60-m x 0.25-mm I.D.; 0.25-um film thickness)
(b) 50-m CP-Sil-88
(c) 30-m SP-2250

5.1.3 Mass Spectrometer: A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions (simultaneously) with a cycle time of 1 second or less. Minimum integration time for SIM is 50 ms per m/z. The use of systems not capable of monitoring 11 ions simultaneously will require the analyst to make multiple injections.

5.1.4 GC/MS Interface

Direct Interface of column exit into source:

Transfer Line Temp:	300°C
Source Temp:	265°C
Analyzer Temp:	250°C

5.1.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot is defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance in any SICP, between specified time or scan number limits.

5.2 Pipets-Disposable, Pasteur, 150-mm long x 5 mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

5.2.1 Pipet, disposable, serological 10 ml (American Scientific Products No. P4644-10 or equivalent) for preparation of the carbon column.

5.3 Reacti-vial 2 ml, amber glass (Pierce Chemical Company). These should be silanized prior to use.

5.4 Filter paper, 18 cm circles.

6.0 REAGENTS AND STANDARD PREPARATION

6.1 Prepare stock standards in a glove-box from concentrates or neat materials. The stock solutions and standards are stored in an isolated refrigerator at 4°C and protected from light and then checked frequently for signs of degradation or evaporation especially just prior to the preparation of working standards. Calibration standard solutions must be replaced routinely after six month.

The method for standards preparation is described in detail in ETC SOP number EX600600, Preparation of Standards for PCDX analysis.

6.2 Calibration Standards (CALSTDS)

6.2.1 Five levels of standards for initial calibration are required as follows:

Analyte	Function	CC1	CC2	CC3	CC4	CC5
2378-TCDD	Native	0.2	0.5	1.0	2.0	5.0
12378-PCDD	Native	0.2	0.5	1.0	2.0	5.0
123678-HXCDD	Native	0.2	0.5	1.0	2.0	5.0
1234678-HPCDD	Native	0.2	0.5	1.0	2.0	5.0
12346789-OCDD	Native	0.2	0.5	1.0	2.0	5.0
2378-TCDF	Native	0.2	0.5	1.0	2.0	5.0
12378-PCDF	Native	0.2	0.5	1.0	2.0	5.0
123478-HXCDF	Native	0.2	0.5	1.0	2.0	5.0
1234678-HPCDF	Native	0.2	0.5	1.0	2.0	5.0
12346789-OCDF	Native	0.2	0.5	1.0	2.0	5.0
37C142378-TCDD	SURR	0.06	-	0.12	-	0.20
13C122378-TCDD	ISTD	0.5	0.5	0.5	0.5	0.5
12C12123678-HXCDD	ISTD	0.5	0.5	0.5	0.5	0.5
13C1212346789-OCDD	ISTD	1.0	1.0	1.0	1.0	1.0
13C122378-TCDF	ISTD	0.5	0.5	0.5	0.5	0.5
13C121234678-HPCDF	ISTD	0.5	0.5	0.5	0.5	0.5
13C121234-TCDD	RSTD	0.5	0.5	0.5	0.5	0.5
13C12123789-HXCDD	RSTD	0.5	0.5	0.5	0.5	0.5

6.2.2 Performance Check Standard (PCSTD)

The column performance check solution contains 6 unlabeled TCDD isomers and the labeled recovery standard. The mixture is used to verify chromatographic separation and demonstrate TCDD isomer resolution. The mixture, which is commercially obtained from Cambridge Isotope Laboratories, contains the following compounds:

1,2,3,4 TCDD 10 ug/ml
1,2,3,7 TCDD 10 ug/ml
1,2,3,8 TCDD 10 ug/ml
1,2,7,8 TCDD 15 ug/ml
1,4,7,8 TCDD 15 ug/ml
2,3,7,8 TCDD 10 ug/ml
1,2,3,4 TCDD 10 ug/ml (C^{13})

6.2.3 Window STD

6.2.3.1 Contains 8 pairs of isomers, one pair for each tetra-through dioxin/furan congener group. Each pair of isomers consists of the earliest and latest eluting isomer for a specific congener. This standard is used to define the retention time "windows" in which the dioxin/furan native compounds will appear.

6.3 Spiking Standards

6.3.1 PCDX SURR/ISTD Spike (SP2)

Compound	Concentration
$^{13}C_{12}$ 2,3,7,8-TCDD	0.5
$^{13}C_{12}$ 1,2,3,6,7,8-HXCDD	0.5
$^{13}C_{12}$ - OCDD	1.0
$^{13}C_{12}$ 2,3,7,8-TCDF	0.5
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF	0.5

Spiked into each sample and replicate.

6.3.2 Blank and Matrix Spike Solution (SP1)

Compound	Concentration
2,3,7,8-TCDD	0.5
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.5
1,2,3,4,6,7,8-HpCDD	0.5
1,2,3,6,7,8-OCDD	1.0
2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.5
1,2,3,4,6,7,8,9-OCDF	0.5

$^{13}C_{12}$ 2,3,7,8-TCDD	0.5
$^{13}C_{12}$ 1,2,3,6,7,8-HXCDD	0.5
$^{13}C_{12}$ - OCDD	1.0
$^{13}C_{12}$ 2,3,7,8-TCDF	0.5
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF	0.5

Spiked into each blank and matrix spike.

6.3.3 Recovery Standard (RSTD)

The recovery standard is spiked into each extract (samples, blanks, and spikes) prior to GC/MS analysis to determine recovery of internal standards.

Compound	Concentration (ug/ml)
$^{13}C_{12}$1234-TCDD	10
$^{13}C_{12}$123789-HxCDD	10

7.0 **INSTRUMENT SETUP AND CALIBRATION**

7.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/ml. (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraph 6.3 and 6.6 is demonstrated and documented.

7.2 Initial GC/MS setup. Establish operating parameters for the GC/MS system; the instrument must be tuned to meet the isotopic ratio criteria listed in the table in Sec 7.1.3 for PCDD's and PCDF's. Do not proceed with calibration and analysis if this isotopic criteria is not achieved.

7.2.1 Chromatographic Conditions

7.2.1.1 For 2,3,7,8-TCDD: 50m CPSil-88 Column

Injector port:	300°C
Oven Temp 1:	150°C
Oven Time:	1.0 min.
Oven Temp Rate 1:	4.0°C/min.
Oven Temp 2:	235°C
Oven Time:	20 min.

7.2.1.2 Alternative Conditions for 2,3,7,8-TCDD:

60m x .25 mm x .25 u film FSOT DB-5 column
Same temperature conditions as in 7.1.1.1.

7.2.1.3 Conditions for tetra- through octa- PCDX, 2,3,7,8-substituted specific:

60m x .25 mm x .25 u film FSOT DB5 column

Injector port:	300°C
Oven Temp 1:	150° min.
Time 1:	1 min.
Oven Temp Rate 1:	4°C/min.
Oven Temp 2:	240°C
Time 2:	7.5 min.
Oven Temp Rate 2:	30°C/min.
Oven Temp 3:	340°C min.
Time 3:	24 min.

7.2.2 Mass Spectrometer Operational Parameters for 2,3,7,8-TCDD:

MS Scan Parameters
Start/Stop
20.00 40.00

MZ	**Dwell (milliseconds)**
257.0	100
259.0	100
320.0	100
322.0	100
328.0	100
332.0	100
334.0	100

7.2.3 Mass Spectrometer Operational Parameters for all other PCDX analyses. Establish selected ion monitoring groups as follows:

Group 1		**Group 2**		**Group 3**		**Group 4**		**Group 5**	
Start/Stop		Start/Stop		Start/Stop		Start/Stop		Start/Stop	
20.00 30.00		33.04 35.65		35.65 37.53		37.53 39.72		39.72 42.72	
MZ	Dwell	MZ	Dwell	MZ	Dwell	MZ	Dwell	MZ	Dwell
243.0	25	277.0	25	277.0	25	311.0	25	345.0	25
[illegible]57.0	25	293.0	25	293.0	25	327.0	25	361.0	25
[illegible]59.0	25	311.0	25	311.0	25	345.0	25	379.0	25
277.0	25	320.0	25	327.0	25	361.0	25	395.0	25
293.0	25	322.0	25	338.0	25	372.0	25	406.0	25

304.0	25	327.0	25	340.0	25	374.0	25	408.0	25
306.0	25	338.0	25	354.0	25	376.0	25	410.0	25
316.0	25	340.0	25	356.0	25	388.0	25	420.0	25
318.0	25	342.0	25	372.0	25	390.0	25	422.0	25
320.0	25	354.0	25	374.0	25	392.0	25	424.0	25
322.0	25	356.0	25	376.0	25	402.0	25	426.0	25
328.0	25	358.0	25	388.0	25	404.0	25	436.0	25
332.0	25	372.0	25	390.0	25	406.0	25	438.0	25
334.0	25	374.0	25	392.0	25	408.0	25	442.0	25
338.0	25	376.0	25	402.0	25	410.0	25	444.0	25
340.0	25	388.0	25	404.0	25	420.0	25	458.0	25
354.0	25	390.0	25	408.0	25	422.0	25	460.0	25
356.0	25	392.0	25	410.0	25	424.0	25	470.0	25
376.0	25	410.0	25	424.0	25	426.0	25	472.0	25
410.0	25	446.0	25	446.0	25	480.0	25	514.0	25

Once tuning and mass calibration procedures have been completed, a column performance check mixture containing the isomers listed below should be injected into the GC/MS system:

TCDD	1,3,6,8; 1,2,8,9; 2,3,7,8; 1,2,3,4; 1,2,3,7; 1,2,3,9
PeCDD	1,2,4,6,8; 1,2,3,8,9
HxCDD	1,2,3,4,6,9; 1,2,3,4,6,7; 1,2,4,6,7,9; 1,2,4,6,8,9
OCDD	1,2,3,4,6,7,8,9
TCDF	1,3,6,8; 1,2,8,9
PeCDF	1,3,4,6,8; 1,2,3,8,9
HxCDF	1,2,3,4,6,8; 1,2,3,4,8,9
HpCDF	1,2,3,4,6,7,8; 1,2,3,4,7,8,9
OCDF	1,2,3,4,6,7,8,9

7.2.4 Insure that the following isotopic ratios are achieved:

Selected Ions m/z			Native Relative Intensity
PCDD's	**Native**	**13C**	
Tetra	320/322	(332/334)	0.65 - 0.89
Penta	354/356	(366/368)	0.55 - 0.75
Hexa	392/390	(404/402)	0.69 - 0.93
Hepta	426/424	(438/436)	0.83 - 1.12
Octa	458/460	(454/456	0.75 - 1.01
PCDF's	**Native**	**13C**	
Tetra	304/306	(316/318)	0.65 - 0.89
Penta	338/340	(350/352)	0.55 - 0.75
Hexa	376/374	(388/386)	0.69 - 0.93
Hepta	410/408	(422/420)	0.83 - 1.12
Octa	442/444	(454/456)	0.75 - 1.01

7.2.5 Window Standard

The window standard contains the earliest and latest eluting isomers of each congener group. Inject to establish retention time windows. The window standard must be run prior to all PCDX batches (more specifically - at the beginning of any PCDX sequence file). Scan start/stop times must be adjusted for any chromatographic shifts observed in the window defining mixture.

7.2.6 Performance Check Standard (PC STD)

Contains 6 TCDD isomers. Used to verify instruments separation and resolution capabilities.

7.2.6.1. PC STDs must bracket any samples (including CC2 STD), and must have injection times within 12 hours of each other, i.e., if PC at the beginning of sample run in injected at 11:14, a "post-sample(s)" PC must be injected before 23:14. (NOTE: Average run time for PCDX analysis is 45-50 Min.).

7.2.6.2 Insure that 2,3,7,8- and 1,2,3,4-TCDD are resolved with a valley $\leq$ 25% where

$$\text{Valley \%} = \frac{(X)}{y} \times 100$$

as shown on the ion profile included in the Appendix.

7.3 Initial Calibration

7.3.1 Analyze each of the 5 calibration standards (6.2.1) in triplicate using 2ul injections. All injections of standards, sample extracts and blank extracts must also be made at this injection volume.

7.3.1.1 Acceptable ion sensitivity is verified by achieving a minimum signal-to-noise ration of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/ml calibration standard.

7.3.2 Calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described below. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

Relative response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Area of quantitation ion of the compound of interest.

A_{is}= Area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

C_{is}= Concentration of the internal standard.

C_s = Concentration of the compound of interest.

The concentrations of unknown isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDD of any available 2,3,7,8-X-PeCDD isomer.

Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard (CC1).

7.3.3 Calculate the mean relative response factor and the relative standard deviator from the triplicate determinations of each calibration standard (CC1 and CC5) as follows.

7.3.3.1 Average response factor for triplicate analysis.

$$RRF_T = \frac{\sum_{i=1}^{3} RRF_i}{3}$$

Where:

RRF_i = The response factor for the calibration standard from an individual determination.

RRF_T = The average response factor for the triplicate analysis.

7.3.3.2 Relative Standard Deviation

$$RSD_T = \frac{\dfrac{\sum_{i=1}^{3} (RRF_i - RRF_T)^2}{2}}{RRF_T} \times 100$$

Where:

RSD_T = Relative standard deviation for the triplicate analysis
RRF_i = Defined as above
RRF_T = Defined as above

7.3.3.3 The relative standard deviation for the triplicate analysis must not exceed 15%. Perform corrective action before proceeding with analysis if this criteria is not achieved.

7.3.4 Calculate the mean response factor and the relative standard deviation for each individual standard for the entire calibration curve as follows:

7.3.4.1 Average response factor for the complete calibration range (CC1 - CC5).

$$RRF_{cal} = \frac{\sum_{i=1}^{5} RRF_{T(i)}}{5}$$

Where:

RRF_{cal} = Mean response factor for the calibration range for an individual analyte.

$RRF_{T(i)}$ = The average response factor for the triplicate analysis of the individual standard from 7.3.3.1.

7.3.4.2 Relative Standard Deviation for the calibration range.

$$RSD_T = \frac{\dfrac{\sum_{i=1}^{5} (RRF_{T(i)} - RRF_{cal})^2}{4}}{RRF_{cal}}$$

Where:

RSD_{cal} = Relative standard deviation for the calibration range

$RRF_{T(i)}$ = Defined as above (7.3.4.1)

RRF_{cal} = Defined as above (7.3.4.1)

7.3.4.3 The relative standard deviation for the calibration curve must not exceed 15%. Perform corrective action before proceeding with analysis if this criteria is not achieved.

7.4 Continuing Calibration

Continuing calibration consists of analyzing the column performance check solution and a concentration calibration solution of .500 ng/uL (500 ppb). No samples are to be analyzed until acceptable calibration is demonstrated and documented.

7.3.1 Inject a 2 ul aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of the 12 hour period. If the contractor laboratory operates during consecutive 12 hour periods (shifts), analysis of the performance check solution at the beginning of each 12 hour period and at the end of the final 12 hour period is sufficient.

Determine and document acceptable column performance as described in Paragraph 7.1.5.2.

7.4 Inject a 2 ul aliquot of the calibration standard solution (CC2 STD) at 500 ng/ml at the beginning of the 12 hour period. Determine and document acceptable calibration as specified (sensitivity and relative ion abundance). The measured RRF's of all analytes must be within $\pm$ 30 percent of the mean values established by initial analyses of the calibration standard solutions.

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank that all glassware and reagents are interferant-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

8.2 A laboratory "method blank" must be run along with each analytical batch (20 or few samples).

8.3 GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12 hour period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

8.4 Accuracy and Precision

8.4.1 Recovery from a blank spike for all analytes must be within 60% to 140%.

8.4.2 Recovery of internal standards in all samples must be within 40% and 120%.

8.4.2.1 If the recovery of any internal standard is outside the criteria, the sample must be re-extracted and re-analyzed.

8.4.3 Recovery from matrix spike for all analytes must be within 60% and 140%.

8.4.4 Replication of duplicate samples must be less than 50% RPD for 2,3,7,8-TCDD. The replication requirements of other PCDX is being developed.

8.5 Summary of QC Samples

Each analytical batch must containing the following QC samples:

8.5.1 Method Blank

8.5.2 Blank Spike

8.5.3 Matrix Spike

8.5.4 Matrix Spike Duplicate

9.0 GC/MS ANALYSIS

9.1 Prior to the analysis of any standard or sample, clip the injector end of the column, removing approximately 1.5 to 2.0 inches of the column. Change the injector liner and the injector septum. Heat the oven to 300°C.

9.2 Tune the instrument in MSCAL. Adjust the parameter to tune as follows:

69 - 100%
219 - 85%
502 - 2-3%

9.3 Begin the analytical sequence with a PC and CC_2 (Continuing calibration). Check the percent valley in PC for 1,2,3,4 and 2,3,7,8-TCDD. The two peaks must be resolved with a valley of $\leq$25% as in 7.1.5.

9.4 Check RRF's in continuing calibration standard. The measured RRF's of all analytes must be within $\pm$30% of the mean values established by initial calibration standard. Check for SIM sensitivity which must meet 50:1 signal to noise ratio for 2,3,7,8-TCDD. Check for relative ion abundance which must meet the criteria (7.1.2).

9.5 Run a window standard to set the retention time window for each congener.

9.6 Approximately one hour before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial. Add to this sufficient recovery standard (5ul of $^{13}C_{12}$1,2,3,4-TCDD and 5 ul of $^{13}C_{12}$123789-HxCDD) to give a concentration of 500 ng/ml. The concentration of the recovery standards in the sample extract must be the same as that in the calibration standards used to measure the response factors.

9.7 Analyze samples and standards with selected ion monitoring, using all of the ions listed in 7.3.2. It is recommended that the GC/MS run be divided into the five selected ion monitoring groups identified in 7.3.2.

9.8 It is recommended that selected ion monitoring section 1 should be applied during the GC run to encompass the retention window of the first and last eluting tetra-chlorinated isomers. If a response is observed at m/z 340 or 356, then the GC/MS analysis must be repeated; selected ion monitoring section 2 should then be applied to encompass the retention window of the first and last eluting penta-chlorinated isomers. **NOTE:** HxCDE, HpCDE, OCDE, NCDE, DCDE, are abbreviations for hexa-, hepta-, octa-, nona-, and decachlorinated diphenyl either, respectively.

9.9 Identification Criteria for PCDD's and PCDF's

9.9.1 All of the characteristic ions, i.e., quantitation ion, confirmation ions, listed above for each class of PCDD and PCDF, must be present in the reconstructed ion chromatogram. It is desirable that M - COCl ion be monitored as an additional requirement. Detection limits will be based on quantitation ions within the molecules in cluster.

9.9.2 The maximum intensity of each of the specified characteristic ions must coincide within 2 scans or 2 seconds.

9.9.3 The relative intensity of the selected, isotopic ions within the molecular cluster of a homologous series of PCDD's of PCDF's must lie within the range specified above.

9.9.4 The GC peaks assigned to a given homologous series must have retention times within the window established for that series by window standard solution.

10.0 CALCULATIONS

10.1 Determine the concentration of individual PCDD/PCDF isomers using the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

Where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted

A_s = are of quantitation of the compound of interest

A_{is} = Response factor of the quantitation ion of the compound of interest relative to m/z quantitation ion of ^{13}C labeled internal standard

NOTE: Any dilution factor should be applied to this calculation.

10.2 The concentrations of detected isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determinate for 1,2,3,7,8-PeCDD and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 1,2,3,6,7,8-HXCDD.

The concentrations of unknown isomers of HxCDD shall be calculated using the mean RRF determined for 1,2,3,4,7,8-HxCDD and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 1,2,3,6,7,8-HXCDD.

The concentration of unknown isomers of HpCDD shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDD and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 1,2,3,6,7,8-HXCDD.

The concentration of unknown isomers of TCDF shall be calculated using the mean RRF determined for 2,3,7,8-TCDF and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 2,3,7,8-TCDF.

The concentration of unknown isomers of PeCDF shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer the internal standard $^{13}C_{12}$ 2,3,7,8-TCDF.

The concentration of unknown isomers of HxCDF shall be calculated using the mean RRF determined for 1,2,3,6,7,8-HpCDF and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF.

The concentration of unknown isomers of HpCDF shall be calculated using the mean RRF determined for 1,2,3,4,6,7.8-HpCDF and the area of the quantitation ion from the internal standard $^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF.

The concentration of the octa-CDD and octa-CDF shall be calculated using the mean RRF determined for each and the area of the quantitation ion from the internal standard.

10.3 If the concentration of any analyte in any sample falls outside linear range, the sample must be re-extracted and re-analyzed using a smaller sample size.

10.4 Calculate the percent recovery, R_{is}, for each internal standard in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_r \times d\ Q_{is}} = 100\%$$

A_{is} = Area of quantitation ion (m/z 334) of the recovery standard $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to the extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

10.5 Calculation of total concentration of all isomers within each homologous of PCDD's and PCDF's.

Total concentration or PCDF's = Sum of the concentrations of PCDD's the individual PCDD or PCDF isomers.

11.0 METHOD DETECTION LIMIT (MDL)

11.1 The MDL values reported in QR table is calculated from the Maximum Possible Concentration (MPC).

11.2 The MPC is the concentration of the target analyte required to produce a signal with a peak height of 2.5 times the background signal level.

$$MPC = \frac{2.5 \times A_x \times Q_{is}}{A_{is} \times RF_i \times W}$$

Where:

A_x = Peak height of noise of the selected ion

Q_{is} = Quantity (ng) of Internal Standard (I.S.) added to the sample before extraction.

W = Weight (g) of volume (L) of sample extracted

11.3 MPC is automatically calculated by procedure file PH#2.

Where # = Instrument ID

11.4 The program calculates MPC based on a few noise peaks in the selected window. The MPC is reported as the MDL for all PCD and PCDFs.

12.0 SUPPLEMENTAL DOCUMENTS AND REFERENCES

12.1 Test Methods for Evaluating Solid Waste, SW-846 Third Edition, November 1986. Method 8280, Revision 0.

12.2 ETC Safety Manual

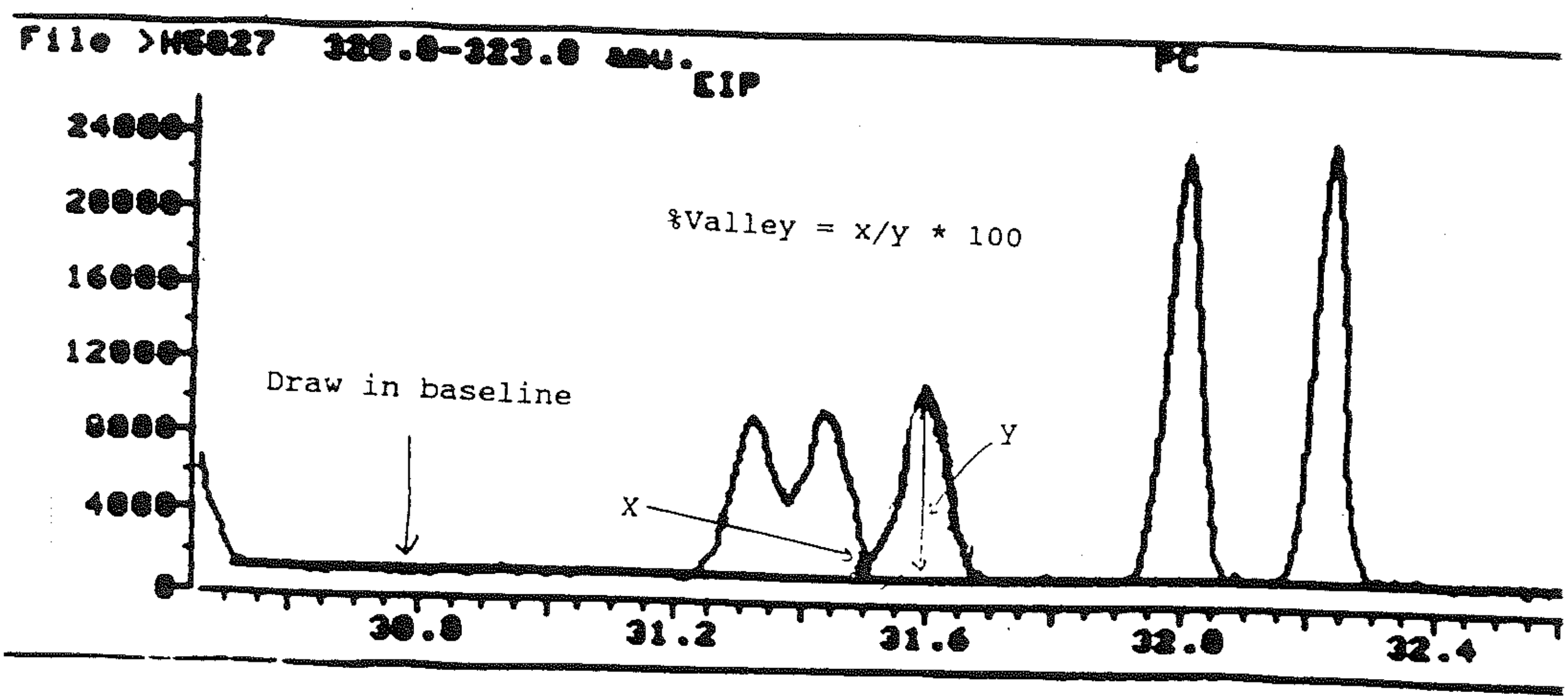
12.3 ETC Sample and Hazardous Waste Disposal SOP #ED201001, or latest revision.

12.4 The Preparation of Standard Solutions for PCDD/PCDF Analysis by SW-846, SOP number EX600600, or latest revision.

12.5 The Extraction and Cleanup of Environmental Waste Samples for PCDD/PCDF Analysis by SW-846, ETC SOP number EX411900, or latest revision.

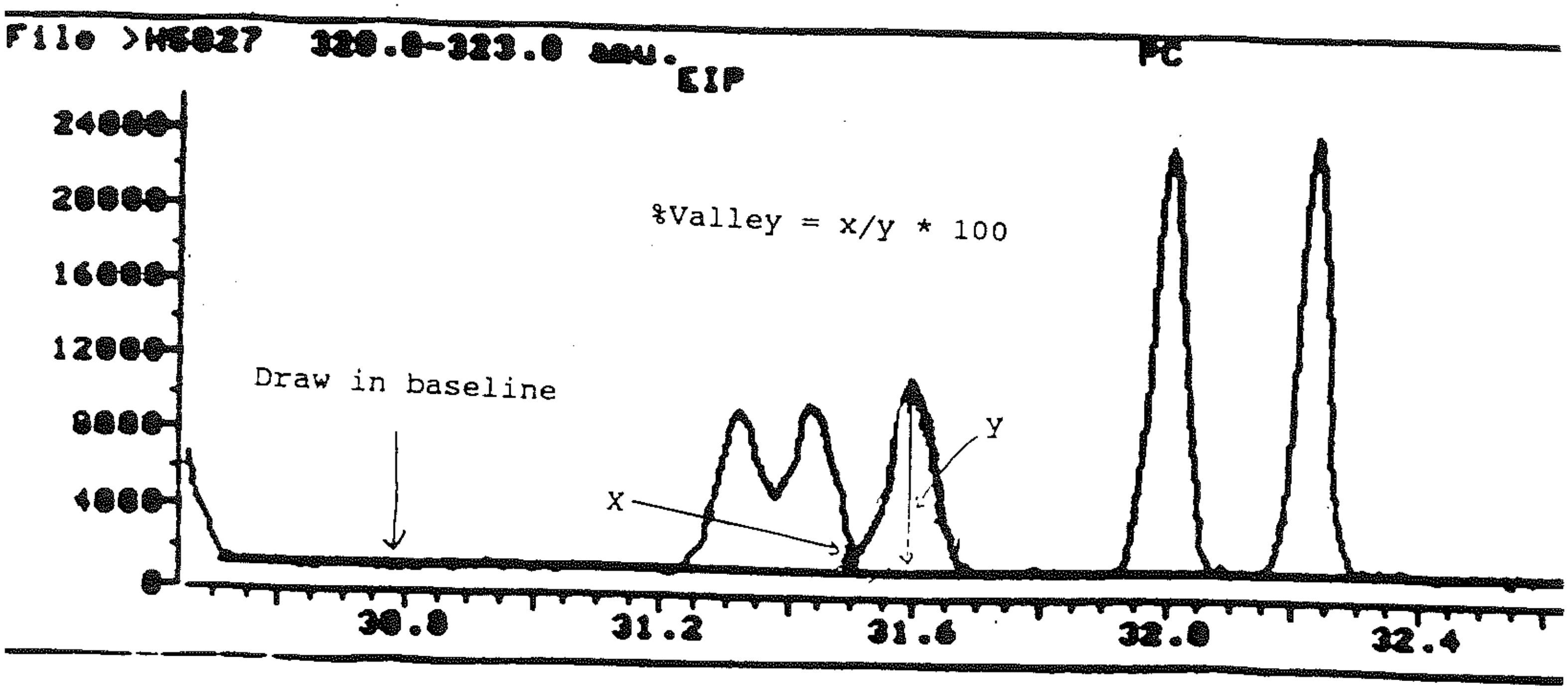
Edits and Annotations
K. Fleming, PACE/NJ
8/9/95

Attachment 7.2.6.2 Ion Profile Chart



APPENDICES

Attachment 7.2.6.2 Ion Profile Chart



1.0 SCOPE AND APPLICATION

1.1 This SOP describes the method which is applicable for the extraction and cleanup of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and furans (PCDF's) from complex industrial waste samples (including sludges, still bottoms, fly ash, soil, and water) by SW-846 Method 8280.

1.2 Additional extract cleanup techniques beyond those described in SW-846 are included as alternatives for sample extracts which are not amenable to cleanup using SW-846 procedures.

1.3 This SOP is applicable to the following A-Types:

1 AP9/PCDX, 2 AP9/PCDX, 1 PCDX/8280, 2 PCDX/8280, 7 MSL/PCDK, 1 TCDD/2378, 2 TCDD/2378.

1.4 Because of the extreme toxicity of these compounds, the lab technician must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to certain PCDD's or PCDF's. Detailed safety procedures are outlined in section 4.0. Reference the ETC Safety Manual for additional safety information.

2.0 SUMMARY OF METHOD

2.1 This SOP describes matrix specific extraction and cleanup procedures for polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) in complex environmental samples. Solvent extraction procedures are detailed for sludge, fuel oil, still bottoms, fly ash, soil, and water using reflux extraction, soxhlet extraction, jar shaking, and liquid/liquid separatory funnel extraction. Specific extract cleanup procedures including acid and basic extract washing, basic/neutral/acidic silica gel chromatography, alumina liquid chromatography, and carbon column liquid chromatography, are described for various "interferents" which may be co-extracted from the sample.

2.2 Method selection is based on the analysts judgement of matrix type and the constituency of co-extracted interferents.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic date. All these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents help to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as polychlorinated biphenyls (PCB's) and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest.

3.4 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

4.0 SAFETY

4.1 Material Safety Data Sheets (MSDS) are available for the chemicals used in the laboratory. All personnel who handle chemicals must know where this information is maintained and must be familiar with the MSDS information.

4.2 All personnel must have attended safety training prior to performing operations in the laboratory in accordance with the laboratory Chemical Hygiene Plan (CHP) as per 29 CFR.

4.3 Any individual who enters a posted area of the laboratory must wear safety glasses with side shields.

4.4 Any individual who handles samples and/or chemicals must wear a laboratory coat and the appropriate gloves for the operation being performed.

4.5 All laboratory areas must be maintained in a neat and orderly fashion. Good housekeeping practices must be employed throughout the laboratory. Laboratory work surfaces, equipment, and instruments must be kept free of residual chemical and/or sample contamination.

4.6 Human Toxicology

4.6.1 The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 part-per-trillion, but the solubility in various organic solvents ranges from 0.001 percent to 0.14 percent.

4.6.2 On the basis of the available toxicological and physical property data and TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

4.7 Safety Equipment

4.7.1 Safe Lab Practice

PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling any contaminated environmental sample. Well-ventilated, controlled-access laboratories are required, and laboratory personnel entering these laboratories should wear appropriate safety clothing.

4.7.2 Protective Clothing

Eye protection equipment must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, when handling samples.

4.7.3 Other Lab Safeguards

Benches and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing.

4.8 Disposal

All laboratory ware, safety clothing, and other items potentially contaminated with PCDD and PCDF in the course of analyses must be carefully secured and subjected to proper disposal. Refer to ETC SOP for the Disposal of Laboratory Wastes number ED201001 for additional information.

5.0 **APPARATUS AND MATERIALS**

5.1 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon.

5.2 Water bath--heated, with concentric ring cover, capable of temperature control ($\pm 2^{\circ}C$). The bath should be used in a hood.

5.3 Pipets-Disposable, Pasteur, Borosilicate glass; 9 inch.

5.3.1 Pipet, disposable, serological 10 ml.

5.4 Amber glass bottle (250 ml Teflon-lined screw-cap).

5.5 Reacti-vial 2 ml, amber glass. Silanized prior to use.

5.6 500 ml Erlenmeyer flask fitted with Teflon stoppers.

5.7 Wrist Action Shaker.

5.8 125 ml and 2 L Separatory Funnels.

5.9 500 ml Kuderna-Danish fitted with a 25 ml concentrator tube and 3 ball Snyder column.

5.10 Teflon boiling chips. Wash with hexane prior to use.

5.11 300 mm x 10.5 mm glass chromatographic column fitted with Teflon stopcock.

5.12 50 ml conical concentrator tubes.

5.13 Adapters for concentrator tubes (14/20 to 19/22).

5.14 Nitrogen blowdown apparatus (N-Evap reg. trademark). Teflon tubing connection to trap and gas regulator is required.

5.15 Microflex conical vials .01 ml.

5.16 Filter paper. Glass fiber filters or glass wool plugs are also recommended.

5.17 Solvent reservoir (125 ml) Kontes: Special order item. 12.5 cm diameter, compatible with gravity carbon column.

5.18 250 ml beakers.

5.19 Disposable aluminum weighing boats.

5.20 100 ul gas tight syringes.

5.21 Spatula (stainless steel).

5.22 Waste Vessel (250 ml or larger).

5.23 Glass wool.

5.24 Taping rod (glass, stainless steel or teflon).

5.25 Aluminum foil.

5.26 Red rubber bulbs (1.0 ml).

5.27 Centrifuge tube racks.

5.28 Crimp seal vials 100 ul (microvials).

5.29 Crimp seal caps 11 mm; teflon-lined.

5.30 Crimper 11 mm.

5.31 1000 ul graduated cylinder (Nalgene).

5.32 Soxhlet Extractor

5.33 Condenser (to fit Soxhlet Extractor body)

5.34 Boiling Flask: (500 ml; flat-bottom)

5.35 Heating Mantle set up:

- Heating Mantle
- Heating Mantle Support
- Rheostat
- Multiple Outlet

5.36 Carborundum Boiling Stones

5.37 Cellulose Thimbles

5.38 Spatula (stainless steel)

5.39 Weighing Boats (aluminum)

5.40 Tongs or tweezers

6.0 REAGENTS AND STANDARDS

6.1 PCDD/PCDF Standards

Prepare stock standards in a glovebox using concentrates or neat materials. The stock solutions (50 ppm) are stored in the dark at 4°C, and then checked frequently for signs of degradation or evaporation especially just prior to the preparation of working standards. Reference ETC SOP number EX600600 for the Preparation of Standard Solutions for PCDD/PCDF Analysis by SW-846.

6.1.1 PCDX Internal Standard Spiking Solution (SP2).

Compound	Concentration (ug/ml)
$^{13}C_{12}$2,3,7,8-TCDD	0.5
$^{13}C_{12}$1,2,3,6,7,8-HXCDD	0.5
$^{13}C_{12}$OCDD	1.0
$^{13}C_{12}$2,3,7,8-TCDF	0.5
$^{13}C_{12}$1,2,3,4,6,7,8-HpCDF	1.0

6.1.2 PCDX Recovery Standard (RSTD).

Compound	Concentration (ug/ml)
$^{13}C_{12}$1234-TCDD	10
$^{13}C_{12}$123789-HxCDD	10

6.1.3 PCDX Blank and Matrix Spiking Solution (SP1).

Compound	Concentration (ug/ml)
2,3,7,8-TCDD	0.5
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.5
1,2,3,4,6,7,8-HoCDD	0.5
1,2,3,6,7,8-OCDD	1.0
2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.5
1,2,3,4,6,7,8,9-OCDF	0.5
$^{13}C_{12}$ 2,3,7,8-TCDD	0.5
$^{13}C_{12}$ 1,2,3,6,7,8-HXCDD	0.5
$^{13}C_{12}$ - OCDD	1.0
$^{13}C_{12}$ 2,3,7,8-TCDF	0.5
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF	1.0

6.4 Reagents

6.4.1 Methylene chloride, High purity; distilled in glass.

6.4.2 Activated anhydrous sodium sulfate (Na2So4)

6.4.3 Methanol High purity; distilled in glass.

6.4.4 Hexane; (U.V. grade).

6.4.5 Neutral silica gel (activated) 60/200 mesh store in oven at 130°C.

6.4.6 Acidic Sulfuric Acid (H2SO4) Modified silica gel.

6.4.7 Basic Sodium Hydroxide (NaOH) Modified silica gel.

6.4.8 Super Woelm Alumina I (Neutral) 80/200 mesh stored in a sealed container at room temperature in a desiccator over self-indicating silica gel.

6.4.9 8% Methylene Chloride/Hexane (V/V) blend, high purity; distilled in glass.

6.4.10 60% Methylene Chloride/Hexane (V/V) blend, high purity; distilled in glass.

6.4.11 AX-21 Activated Carbon Mix.

6.4.12 50% (V/V) Methylene Chloride/Cyclohexane (V/V) blend, high purity; distilled in glass.

6.4.13 75/20/5 % (V/V/V) methylene chloride/Methanol/benzene, blend, high purity; distilled in glass.

6.4.14 Zero Grade Nitrogen.

6.4.15 Dodecane (Fluka Chemicals).

6.4.16 Toluene, high purity; distilled in glass

7.0 QUALITY CONTROL

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a reagent blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

7.2 For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

7.3 Accuracy and Precision

7.3.1 Recovery from a blank spike for all analytes must be within 60% to 140%.

7.3.2 Recovery of internal standards in all samples must be within 40% and 120%.

7.3.3 Recovery from matrix spike for all analytes must be within 60% and 140%.

7.3.4 Replication of duplicate samples must be less than 50% RPD for 2,3,7,8-TCDD.

7.4 Summary of QC Sample Spiking Solution Volumes

7.4.1 Method Blank - 100 ul ISTD spike (SP2).

7.4.2 Blank Spike - 100 ul native (SP1)/ISTD spike (SP2).

7.4.3 Matrix Spike - 100 ul native (SP1)/ISTD spike (SP2).

7.4.4 Matrix Spike Duplicate - 100 ul native (SP1)/ISTD spike (SP2).

8.0 SAMPLE PRESERVATION AND HANDLING

8.1 All samples must be stored at 4°C and extracted within 30 days and completely analyzed within 45 days of collection.

9.0 SAMPLE PREPARATION AND EXTRACT CLEANUP

9.1 Extraction Procedures

9.1.1 Sludge/Fuel Oil

9.1.1.1. Extract aqueous sludge samples by refluxing a sample (e.g. 2. g) with 50 ml of toluene (benzene) in a 125 ml flask fitted with a Dean-Stark water separator.

9.1.1.2. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100 ml round bottom flask. Rinse the filter with 10 ml of toluene, combine the extract and rinsate.

9.1.1.3. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.1.

9.1.2 Still Bottoms

9.1.2.1. Extract still bottom samples by mixing a sample (e.g., 1.0 ml of toluene (benzene) in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50 ml round bottom flask.

9.1.2.2. Rinse the beaker and filter with 10 ml of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.1.3.4.

9.1.3 Fly Ash. Any solid sample which has a high carbon content or cannot be extracted using the jar shake approach.

9.1.3.1. Place an appropriately labelled aluminum weighing boat on a calibrated top loading balance, and tare the balance.

9.1.3.2. Accurately weigh approximately 10.0 g of sample into the pan. Record the sample weight to three significant figures on the laboratory chronicle.

NOTE: QC blanks and blank spikes will consist solely of sodium sulfate.

9.1.3.3. Thoroughly mix the 10 gram sample and an equivalent amount of anhydrous sodium sulfate using a spatula and transfer the mix to a cellulose extraction thimble. Place the thimble into an appropriately labelled soxhlet apparatus that has been charged with 250 ml of toluene and contains 8-10 boiling stones in the reservoir.

9.1.3.4. Extract the samples for a minimum of 16 hours at a 3-cycle per hour reflux rate.

9.1.3.5. Allow the soxhlet apparatus to cool completely before removing from heating set-up.

9.1.3.6. Tilt soxhlet set-up to drain any residual toluene from extractor body. Allow any toluene in extractor body to separate from sample and repeat until no more toluene can be withdrawn.

9.1.3.7. Filter the toluene extract through a glass filter paper into a 500 ml round bottom flask. Rinse the filter with 10 ml of toluene.

9.1.3.8. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C.

9.1.3.9. Transfer the residue to a 120 ml separatory funnel using 15 ml of hexane. Rinse the flask with two 5 ml aliquots of hexane and add the rinses to the funnel. Shake 2 min with 50 ml of 5% NaCl solution, discard the aqueous layer and proceed with Step 9.2.

9.1.4 Soil

9.1.4.1. Extract soil samples by placing the sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500 ml Erlenmeyer flask fitted with a Teflon stopper.

9.1.4.2. Add 20 ml of methanol and 80 ml of petroleum ether, in that order, to the flask. Shake on a wrist action shaker for two hours. The solid portion of sample should mix freely. If a small soil aliquot is used, scale down the amount of methanol proportionally.

9.1.4.3. Filter the extract from Paragraph 9.1.4.2 through a glass funnel fitted with an 18.5cm Whatman ashless glass fiber filter and filled with anhydrous sodium sulfate into a 500 ml Kuderna-Danish (KD) concentrator fitted with a 10 ml concentrator tube.

9.1.4.4. Add 50 ml of petroleum either to the Erlenmeyer flask, re-stopper and flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional 50 ml aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional 5 ml portions of petroleum ether.

9.1.4.5. Add a Teflon or PFTE boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C water bath to an apparent volume of 10 ml. Remove the apparatus from the water bath and allow it to cool for 5 min.

9.1.4.6. Add 50 ml of hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 ml. Remove the apparatus from the water bath and allow to cool for 5 min.

9.1.4.7. Remove and invert the Snyder column and rinse it down into the KD with two 1-ml portions of hexane. Decant the contents of the KD and concentrator tube into a 125-ml separatory funnel. Rinse the KD with two additional 5-ml portions of hexane, combine. Proceed with Step 9.3.

9.1.5 Water

9.1.5.1. Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Step 9.1.5.2.

9.1.5.1.1. A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. Add 60 ml of methylene chloride to the sample bottle, seal, and shake for 30 sec to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-ml portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 ml of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.1.4.5 and 9.1.5.3. Proceed with Paragraph 9.1.5.4.

9.1.5.2 Add 60 ml methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 ml) directly into a 500-ml Kuderna-Danish concentrator (mounted with a 10-ml concentrator tube) by passing the sample extracts through a filter funnel fitted with an 18.5cm Whatman ashless glass fiber filter and packed with a glass wool plug and 5 9 of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 ml of methylene chloride to ensure quantitative transfer.

9.1.5.3 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 ml. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 100 ml hexane, re-attach the Snyder column and concentrate to approximately 5 ml. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 ml hexane and combine rinses with extract to five a final volume of about 15 ml.

9.1.5.4 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-ml graduated cylinder. Record the sample volume to the nearest 5 ml. Proceed with Paragraph 9.2.

9.1.6 Alternate Procedure for the Extraction of Sludges, Oil, Tar, and Still Bottoms.

Alternate procedure for the extraction of sludges, oil, tar, and still bottoms (SAS 6179-A, SOW for the Analysis of Polychlorinated Dibenzo-p-Dioxins (PCDD) and Poly-chlorinated Dibenzofurans, 12/90 with published modifications).

9.1.6.1 Characterize the sample matrix to determine its organic solvent solubility.

9.1.6.2 If the sample is soluble in hexane or methanol, proceed with section 9.1.4. with the following modifications:

i. Weigh out 1.00 g (+0.05 g) of sample.

ii. Scale down methanol proportionally, i.e., use 2.0 ml methanol.

9.1.6.3. If the matrix characterization indicates that the sample is soluble in methylene chloride, toluene, or benzene, proceed as follows:

i. Using a properly calibrated top loading balance, place an appropriate labelled 8 oz. clear Boston round bottle on balance pan and tare the balance.

ii. Accurately weigh 1.00 g of sample into the bottle. Record the sample weight to three significant figures on the laboratory chronicle.

iii. Spike with 100 ul of the appropriate spiking solution (internal standards and surrogates, matrix or blank spikes).

iv. Add 100 ml of appropriate extraction solvent (from matrix characterization).

v. Cap securely and shake on wrist action shaker for at least two hours.

vi. Solvent exchange extracts to hexane.

- o Solvent exchange capability is dependent upon solvent boiling point. Lower boiling solvents (methylene chloride, hexane) can be exchanged using a steam bath. Higher boiling solvents (toluene) will require a heating mantle to complete the solvent exchange.

- o On occasion, samples extracts cannot be directly solvent exchanged to hexane -- upon initial concentration the extract will become very viscous and/or begin to polymerize. Should this occur, reconstitute extract in minimal amount of extraction solvent, such that extract is no longer viscous. Proceed as follows:

- Set-up a large bore chromatographic column with teflon stopcock.

- Add approx. 130 ml hexane to column, such that hexane occupies lower third of reservoir bowl.

- Charge column with 20.0 g of activated neutral silica gel.

- Drain into waste vessel until hexane level is just above surface of silica gel. NOTE: Rinse bowl with hexane during draining to wash down any adhered silica gel.

- Place prepared column over appropriate receiving vessel. K-D apparatus for methylene chloride extracts, 500 ml boiling flask for toluene extracts.

- Quantitatively transfer extract to column, using 3 rinses with extraction solvent.

- Elute extract with 250 ml hexane.

- Proceed with solvent exchange (as above) as though extract was in original extraction solvent.

9.2 Extract Cleanup Procedures

Extract cleanup procedures are employed for the removal of co-extracted organic compounds which may be pose interference difficulties during instrumental analysis. Individual cleanup procedures are selected based on the nature of the interfering compounds.

9.2.1 Acid/Base Washing

9.2.1.1. In a 250-ml Separatory funnel, partition the solvent (15 ml hexane) Against 40 ml of 20 percent (weight/volume) potassium hydroxide. Shake for 2 min.

Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a **maximum** of four times). Strong base (KOH) is known to degrade certain PCDD/PCDF's, contact time must be minimized.

9.2.1.2. Partition the solvent (15 ml hexane) against 40 ml of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard aqueous layer (bottom).

NOTE: Care should be taken due to the heat of neutralization and hydration.

9.2.1.3. Partition the solvent (15 ml hexane) against 40 ml of concentrated sulfuric acid. Shake for 2 min. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

9.2.1.4. Partition the extract against 40 ml of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate into a 50-ml round bottom flask, wash the separatory funnel with two 15-ml portions of hexane, pour through the funnel, and combine the hexane extracts. Concentrate the hexane solution to near dryness with a rotary evaporator (35-C water bath), making sure all traces of toluene are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted). Alternatively, employ a KD apparatus to complete the concentration process.

9.2.2 Alumina Column Chromatography. Separation of polar interferents using a gravity column (Glass 300mm x 10.5mm) packed as follows:

9.2.3.1. Insert a glass wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4g layer of Woelm Super 1 neutral alumina. Tap gently to pack and eliminate air spaces. Cover the alumina with a 4-g layer of sodium sulfate.

9.2.3.2. Elute with 10ml of hexane closing the stopcock immediately before exposing the sodium sulfate to the air. Check for column channeling and discard if it has occurred.

9.2.3.3. Re-constitute the residue from the sample extraction step in 2ml of hexane and apply the solution to the top of the column. Elute with sufficient hexane to complete the transfer of the extract onto the column. Discard the eluent.

9.2.3.4. Elute the column with 10 ml of 8% (volume/volume) methylene chloride in hexane to remove impurities. Save the eluent and check for PCDD/PCDF breakthrough (See PCDD/PCDF analysis SOP). Continue the elution with 15 ml of 60% methylene chloride in hexane and collect the eluant in a 15 ml concentrator tube. Dioxins and furans will be contained in this fraction. Retain this fraction for concentration and subsequent GC/MS analysis or additional chromatographic cleanup as required.

9.2.3 Multi-Stage Silica Gel Column (Alternate Procedure)

9.2.3.1. Pack a gravity column (glass 300-mm x 1.8cm I.D. with 250ml reservoir), fitted with a Teflon stopcock, in the following manner:

Insert a glass-wool plug into the bottom of the column. Fill the column with hexane (approx 130ml). Add a 1 gram layer of neutral silica gel, followed by (in order) a 2 gram layer of basic silica gel, a 1 gram layer of neutral silica gel, a 10 gram layer of acid silica gel, and a 2 gram layer of neutral silica gel. Woelm super 1 neutral alumina.

9.2.3.2. Drain the hexane into a waste container stopping just before the uppermost layer of silica gel is exposed. Rinse adhering silica gel from the sides od the column with additional hexane.

9.2.3.3. Prepare a small bore alumina column in the following manner:

Insert a glass-wool plug into the bottom of the column. Add 6.0 grams of acidic alumina, tap to settle. Add 1.0 grams sodium sulfate to the top of the column. Rinse adhering silica gel from the sides of the column with hexane. Continue filling the column with hexane (approx 130ml) until the level reaches the bottom of the reservoir. Drain the hexane into a waste container stopping just before the uppermost layer of silica gel is exposed.

9.2.3.4. Dissolve the residue from Step 9.2.1 in 2 ml of hexane and apply the hexane solution to the top of the silica gel column. Complete the transfer with multiple hexane rinses. Elute the extract with sufficient hexane to complete the transfer of the sample cleanly to the surface of the alumina. Place the reservoir of the alumina column directly below the stopcock of the silica gel column. Rinse the reservoir of the large bore column with 3.0 ml hexane. Again drain the hexane into a waste container stopping just before the uppermost layer of silica gel is exposed.

9.2.3.5. Add 150 ml of hexane to the upper reservoir, open the stop cocks of each column and allow the hexane to completely drain through both columns. Discard the eluate. rinse the reservoir with 2.0 ml of hexane, elute and discard.

9.2.3.6. Add 20.0ml of hexane to the lower (alumina) column, elute to the top of the sodium sulfate layer, and discard the eluant.

9.2.3.7 Replace the waste vessel with a labeled 50 ml concentrator tube. Add 20ml of 20% methylene chloride in hexane to the reservoir of the column and continue the elution. Collect the eluate.

9.2.3.8 Concentrate the methylene chloride/hexane eluate to approximately 2-3 ml using either nitrogen blowdown or micro-KD apparatus.

9.2.4 Carbon Column Cleanup. Separation of planar molecules from PCDD/PCDF.

9.2.4.1. Prepare a micro-carbon column packing by mixing 5% methanol pre-washed, active carbon (AX21, Anderson Development Company) with 95% type 60 EM reagent 70-230 mesh Silica Gel and activating at $130_{0}C$ for 6 hours.

9.2.4.2. Cut off the ends of a 10ml semiological disposable pipette, insert a glasswool plug into the pipette and pack it with 1.0 gram of carbon/silica gel mixture. Cap the carbon column with an additional glass wool plug.

9.2.4.1. Concentrate the 60 percent fraction eluant (Paragraph 9.2.2.4 or 9.2.3.8) to about 2 to 3 ml. Rinse the carbon with 5 ml cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 ml of cyclohexane/methylene chloride (50:50 v/v) and 5 ml of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine (this fraction may be used as a check on column efficiency). Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 ml toluene. Note: Be sure no carbon fines are present in the eluant.

9.2.4.2. Evaporate the toluene fraction to about 1 ml on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0 ml reacti-vial using a toluene rinse and concentrate to 200-300ul using a stream of nitrogen (N-Evap). The final volume should be 100 ul for soil samples and 500 ul for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl in the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

10.0 PACKAGING OF EXTRACTS (100 ul MICROVIALS)

10.1 Packaging Procedures

To eliminate any confusion or switching of extracts it is imperative that extracts and microvials be kept in same numerical order at all times. Always work "top to bottom" and "left to right" when referencing extracts and their containment vessels, i.e. The job number at the top of the lab chronicle is considered the "first" extract and will be placed left-most when handling extracts in a horizontal procedure (e.g column work, N-Evap, packaging, etc...). The bottom job number on the laboratory chronicle is considered the "last" extract and will appear right-most in a horizontal procedure. The intermediate extracts are then placed sequentially from left to right as they are read, going down the laboratory chronicle.

10.1.1 Prepare microvials for receipt of extract by writing job number (using a Sharpie waterproof pen) along length of microvial. "Double-label" the vial by writing job number again on the opposite side of vial.

NOTE: Use black or blue pen only, for ease of reading.

10.1.2 Add 5.0 ul of dodecane to each of the microvials. (The dodecane acts as a "keeper" to prevent the extract from going to dryness). Replace the microvials, in order, into their vial case(s).

10.1.3 Load the extract anti-clockwise onto the nitrogen evaporator (N-Evap) following the order they appear on the laboratory chronicle. Refer to SOP: IFB/PCDX Concentration by Nitrogen Evaporation (N-EVAP).

10.1.4 Concentrate the extracts to approximately 100 ul; remove from N-Evap (leaving pipettes); and place in the containment rack--again in the same order as they appear on laboratory chronicle.

10.1.5 Turn off the nitrogen supply at the plenum knob.

10.1.6 Place a 9" disposable pasteur pipette, fitted with a pipette bulb, into each of the extract containment vessels.

NOTE: The hard-rubber 1.0 ml pipette bulbs are recommended for this procedure, as they are less flexible than latex bulbs and therefore less likely to allow accidental loss of extract.

10.1.7 Carefully place the microvials (in order) on the N-Evap, so that the full width of the vial body is in contact with the support place assembly. The vials should be absolutely vertical--not leaning in any direction.

10.1.8 Lower the corresponding nitrogen-carrying pipette, such that the tip barely intrudes into the vial opening. Position the pipette tip, such that it is located to the rear of the vial (towards center of N-Evap), so that a pipette tip to transfer the extract may be inserted between the nitrogen pipette and the microvial inner-wall.

NOTE: At this point it is best to make two safety checks:

1. Make sure nitrogen is off at plenum knob.
2. Ensure all individual nitrogen ports are open to the same degree (i.e., none partially open, while others fully open).

10.1.9 Carefully transfer the first three extracts from their containment vessels to their respective microvials.

10.1.10 Slowly turn on the nitrogen at the plenum know, while watching the contents of the microvials, to make sure that extracts will not be blown out. The flow of nitrogen onto the surface of the extracts should be barely perceptible.

10.1.11 Complete the transfer of the remaining extracts.

10.1.12 Using a 9" disposable pipette, add 12 drops of hexane or 300 ul to each of the containment vessels.

10.1.13 Starting at a point representing half the initial volume of the extract previously in the containment vessel (i.e., if the extract was at 20 ml before N-Evap, start at 10 ml volume line): Wash the inside walls of the containment vessel in a circular motion, progressively moving downwards with the rinses.

10.1.14 Ensuring the volume in the microvials is low enough to receive the hexane rinse, transfer the rinse from the containment vessels to their respective microvials.

10.1.15 Repeat steps 10.1.12 through 10.1.14; this time beginning the wash at the original extract volume (e.g., from above-- at 20 ml volume line).

10.1.16 Concentrate extract (with rinses) down to a volume of 5.0 ul.

NOTE: The extract will concentrate quite rapidly to a volume of 2-5 ul. At this point, the volume will not appear to decrease appreciably, due to the presence of the dodecane keeper. Remove the microvial from the N-Evap when no further concentrating is evident.

10.1.17 Compare the volume in the microvial to the microvial volume standards in the clear lucite rack. Add an appropriate amount of dodecane to bring the final volume to the mircovial to 20 ul.

10.1.18 Cap the vial, using an 11 mm, teflon-lined crimp cap. Ensure the cap fits tightly, and may not be rotated.

10.1.19 Holding the top of the vial, "Flick" the vial bottom with index finger to mix contents.

10.1.20 Place vial (in proper order) in vial case. Label case with QT-Batch number and GC/MS A-type.

10.1.21 Place samples in GC/MS extract refrigerator for analysis.

10.2 Preparation for Analysis

10.2.1 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial. Add to this sufficient recovery standard (13C121,2,3,4-TCDD) to give a concentration of 500 ng/ml. (Example: 36 ul aliquot of extract and 4 ul of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 ul) of the sample into the GC/MS instrument.

11.0 SUPPLEMENTAL DOCUMENTS AND REFERENCES

11.1 Test Methods for Evaluating Solid Waste, SW-846 Third Edition, November 1986. Method 8280, Revision 0.

11.2 ETC Safety Manual

11.3 ETC Sample and Hazardous Waste Disposal SOP #ED201001

11.4 The Preparation of Standard Solutions for PCDD/PCDF Analysis by SW-846, SOP number EX600600.

GEOTECHNICAL LABORATORY TESTING CAPABILITIES

Index Properties:

- visual classification and water content
- grain-size distribution
- organic content
- reactive sulfate
- total carbonate content
- liquid, plastic and shrinkage limits
- specific gravity
- pH level
- total salt content
- cation exchange capacity

Compaction Testing:

ASTM methods are used to determine the moisture-density relationships for soils to be used in fill placement. Both mechanized and hand-operated compactors are available as may be required to provide specified compaction energy levels.

Permeability:

The laboratory is equipped to perform constant-head and falling-head permeability tests by the appropriate ASTM standards. Both flexible-wall and fixed-wall cells are available. Twenty back-pressure saturation and consolidation stations are used to perform the falling-head tests. Five of these stations are constant- flow stations which use mercury manometers for precise measurement of pore water movement through low-permeability clays and geosynthetic clay liner materials.

Compressibility:

One-dimensional consolidation properties are obtained using fixed-weight loading frames. These frames may be monitored using automated data acquisition equipment. Controlled rate-of-deformation consolidation tests may be performed using specially adapted triaxial cells.

Static Strength:

The laboratory is equipped to perform unconfined and triaxial compression testing of soil and rock specimens. Triaxial cells manufactured by Brainard-Kilman and Trautwein Equipment are used for specimen diameters up to 4-in.-diameter (100 mm) specimens and effective confining pressures up to 120 psi (830 kPa). Twenty back-pressure saturation/consolidation stations are available.

GEOTECHNICAL TESTING CAPABILITIES
Rust Cincinnati Division

Test	Sample Size inches (mm)	Maximum Pressure Limits, psi (kPa)	Applicable ASTM Standard	Comments
Triaxial Compression	Diameters: 1.5 to 4 (38 to 100)	Cell Pressure: 120 (830)	D2850 D4767	Unconsolidated-Undrained Consolidated-Undrained
Unconfined Compression	Diameters: 1.5 to 4 (38 to 100)	N/A	D2166	
Direct Shear	Diameter or Width: 2.0 to 12.0 (50 to 305)		D3080	
Consolidation Incremental Controlled-Strain	Diameters: 2.5 to 4 (63 to 100)	350 (2450)	D2435 D4186	Dead-Weight Load Frame
Permeability Constant Head Falling Head	2 to 4 (50 to 100) 1.5 to 4 (38 to 100)		D2434 D5084	
Liquid and Plastic Limits			D4318	
Specific Gravity			D854	
Moisture Content			D2216	
Grain-Size Aggregate Sieve Hydrometer			D422 D422	Controlled Temperature Bath
Organic Content			D2974	
Compaction	4 and 6 (100 and 150)		D698 D1557	Mechanical Compactor

ADDITIONAL EQUIPMENT (Field Testing):

- RocTest Pressuremeter
- Troxler Nuclear Density Gauges
- HydroPunch

Geotechnical Laboratory Division
RUST Environment & Infrastructure

SOP Number: SOP-GT-001
Effective: July, 1995
Revision: 1

STANDARD OPERATING PROCEDURE FOR RECEIVING INCOMING SAMPLES

STEP 1

Log sample into Sample Log Book, include project name, number, client, sample number, location and testing required, assign a number to the Assignment Sheet and date received.

- Alternatively, the Soil Request Records may be used as the Sample Log Book (currently used in Baton Rouge).

STEP 2

After completing the Log-in process, place the sample to be tested in the appropriate testing area, i.e., Proctors, Classifications, Strength and Permeability, etc.

STEP 3

Complete all required project information on each data sheet including sample locations, stations, elevation, numbers, etc.

STEP 4

If separate, setup the soil laboratory worksheet. Include all information as completed in Step 1. Circle all required testing and any special information that may have been supplied by the project, Project Manager or other. Place the Soil Laboratory Worksheet with the sample.

Prepared by: B. M. Griggs 3/30/95
Reviewed by: Kirk Lowery 11/10/95
Approved by: Kirk Lowery 11/14/95

STANDARD OPERATING PROCEDURE FOR PROCESSING BULK SAMPLES

STEP 1

Set up Soil Laboratory Worksheet. See SOP-GT-001, Step 4 for reference. Weigh entire content of the bulk sample and record in Remarks Section on worksheet.

STEP 2

Lay out entire sample on a flat pan in proctor area.

STEP 3

Completely fill out two sample tags and place one with sample and one on a bucket for use later. Include project name and number, sample number or I.D. Collect approximately 1500 grams for sieve analysis, place into bucket or flat pan and set aside.

STEP 4

Collect a representative 300-500 gram sample for Natural Moisture Content (NMC) prior to any drying of the bulk sample. Place into a sealed plastic bag and leave with bulk sample. (The NMC sample may be used for P-200, See SOP-GT-07.4).

NOTE: Should the bulk sample be in excess of 10% greater than the estimated Optimum Moisture Content (OMC), allow the entire bulk sample to air dry until the moisture content has been reduced to about 6% greater than the estimated OMC. Then proceed with STEP 5.

STEP 5

Dice and chop bulk sample in the flat pan and remove, weigh and record on worksheet any large stones; place bulk samples into the Rapid Soil Processor. Make the necessary hook-ups on the Soil Processor. Place the larger black tub under, and the smaller black tub towards the back of the Soil Processor. Turn on the Soil Processor and allow it to shave the entire bulk sample until all the soil has been "Processed". USE CAUTION!

STANDARD OPERATING PROCEDURE FOR PROCESSING BULK SAMPLES (continued)

STEP 6

From the Processed Bulk Sample, collect about 200 grams of moist soil for Atterberg and place into a marked container. Record container's ID on worksheet in Atterberg Limits Section. Place distilled water in container covering soil and place in classification testing area of the laboratory.

STEP 6.1

From the Processed Bulk Sample, collect approximately 200 grams of moist soil for the hydrometer analysis (Wet Method) and place into a marked container. Record container ID on worksheet in Hydrometer Section. Place distilled water in container covering soil and place in classification testing area.

STEP 7

Check worksheet for completeness. Leave worksheet with bulk samples.

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Approved by: Kirk Lowery 11/14/95

Geotechnical Laboratory Division
RUST Environment & Infrastructure

SOP Number: SOP-GT-005
Effective: July, 1995
Revision: 1

STANDARD OPERATING PROCEDURE FOR ASTM D4318 - ATTERBERG LIMITS (Wet Method)

STEP 1

Complete all project information on the data sheet.

STEP 2

Collect 200 gms from the processed bulk sample - see SOP-GT-002, Step 5, or place the 200 gms into a marked container and place tap or distilled water into the container just covering the soil. Allow to soak until mixing. Mix the material in the blender for 1 minute. Pour the soil/water mixture over a #40 sieve which has been previously placed on top of a oven dried "Dog Bowl". Allow soil slurry to dry until a thick paste has developed. Collect approximately 40 grams of this material for plastic limits and place this sample to the side for testing later.

STEP 3

Calibrate drop of liquid limit cup using the grooving tool handle. Place approximately 150 gms of the soil into a mixing dish and thoroughly mix. Spread soil into the liquid limit cup approximately 10 mm thick. Cut a grove through the center of the filled cup using the grooving tool. Turn the handle on the limit cup at a rate of about two blows (drops) per second and count the number of blows (drops) of the limit cup required to close the grove between the two halves approximately ½ inch. Point one should require 20 to 30 blows to close the groove. Collect a sample of this material perpendicular to and across the closed groove and place in a tare. Cover tare until wet weight plus tare is determined.

STEP 4

Repeat the above steps one additional time for verification of point one. After completing both points of the liquid limit, weigh and record the weight of both samples plus tare on the data sheet and place them in the drying oven.

STANDARD OPERATING PROCEDURE FOR ASTM D4318 - ATTERBERG LIMITS (Wet Method) (continued)

STEP 5

Take the plastic limit samples and roll them out on a glass plate. Continue rolling and kneading until the soil sample can no longer be rolled out to an 1/8" thread. Collect 2 samples of this rolled out material and place in a tare (approximately 12 gms each). Weigh and record the weight of each sample and tare and place them in the drying oven.

STEP 6

Check the data sheet for completeness.

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Approved by: Kirk Lowery 11/14/95

Geotechnical Laboratory Division
RUST Environment & Infrastructure

SOP Number: SOP-GT-007
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Revision: 2

STANDARD OPERATING PROCEDURE FOR SOIL CLASSIFICATION - GRAIN SIZE ANALYSIS OF SOIL ASTM D422

STEP 1

Complete all project information on the soil classification data sheet.

STEP 2

Oven dry at least 1,500 grams or the appropriate weight depending on maximum particle size, obtained from the bulk or tube sample. Place sample into container for drying. Record the container's I.D. number on the soil classification data sheet, grain size section.

NOTE: All Hydrometers Samples Shall be Tested using the Wet Method, SOP-GT-07.2 , unless instructed otherwise, inwhich case, use SOP-GT-07.1.

STEP 3

After drying, record dry weight of sample minus any tare weight on worksheet. Place sample into Beaker or Plastic Bucket. Record container's Id on worksheet and cover sample with tap water in container. Allow sample to soak.

STEP 4

After soaking, agitate sample in container using a wire wisp. Wash thoroughly over a # 10 sieve or # 200 sieve depending on type of test, see note.

NOTE: If Hydrometer is in progress, wash over # 10 sieve. If a grain-size with # 200 wash has been requested, wash sample over a # 200 sieve.

STANDARD OPERATING PROCEDURE
FOR
SOIL CLASSIFICATION - GRAIN SIZE ANALYSIS OF SOIL ASTM D422
(continued)

STEP 5

After washing, return sample to tare and place into over for drying. Record tare Id on worksheet.

STEP 6

After drying, pass the soil over a nest of sieves as: $1^1/_2$, 1, $^3/_4$, $^1/_2$, $^3/_8$, $^1/_4$, #4 and #10 (# 40 and # 200 if a grain-size with wash # 200 has been requested).

Record the weights of the material retained on each sieve cumulatively. Once the total weight retained on the #10 or # 200, has been determined and recorded, place sieved sample into a labeled plastic bag. <u>DO NO DISCARD SAMPLE</u>. Check the data sheet for completeness. Return paperwork to the Hydrometer Testing Area or Data Reduction Basket.

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Revised by: B. M. Griggs 4/01/96
Reviewed by: Kirk Lowery 4/01/96
Reapproved by: Kirk Lowery 4/03/96

STANDARD OPERATING PROCEDURE FOR ASTM D2216 - NATURAL MOISTURE CONTENT

STEP 1

Complete all project information on the data sheet.

STEP 2

Collect 50 to 1500 gms of wet sample depending on particle size of sample and place in tare. Weigh wet soil and tare. Record weight on data sheet. Place tare and sample in drying oven.

STEP 3

Leave data sheet in basket next to oven.

NOTE: This specimen may be used for P-200, see SOP-GT-07.4.

Geotechnical Laboratory Division
RUST Environment & Infrastructure

SOP Number: SOP-GT-07.1
Effective: July, 1995
Revision: 1

STANDARD OPERATING PROCEDURE FOR ASTM D422 - HYDROMETER ANALYSIS (Dry Method)

STEP 1

Complete all project information on the data sheet. Riffle split 200 gms from the 1500 gm sample obtained from the Proctor area. Pulverize sample using a mortar and pestel and pass material over a #10 sieve. Discard the plus #10 material. (See SOP-GT-003, Step 2 for reference).

STEP 2

Mix the minus #10 material and collect a 50 gm sample for hygroscopic moisture. Obtain and record weight of soil and tare and place in drying oven. Collect 50-70 gms of minus #10 material for hydrometer testing. Record sample and tare weight on data sheet. Mix this 50-70 sample with 125 ml of hydrometer solution and allow to soak at least 16 hours.

STEP 2.1

Prepare a control flask consisting of distilled water and 125 ml of hydrometer solution which is at the same temperature as the Hydrometer test specimen. From the control flask, the composite correction and temperature readings will be obtained during the Hydrometer test.

STEP 3

After soaking, pour soil/solution mixture into the blender and mix for 1 minute. After 1 minute of mixing, transfer soil/solution mixture into hydrometer flask. Use a squirt bottle to remove all soil from the blender. Fill the hydrometer flask to just below the fill line with distilled water and the soil/solution mixture. Thoroughly mix the distilled water and soil/solution mixture by inverting and reversing the flask for 1 minute. Wash down any remaining soil on the sides of the flask and bring the water level (bottom of the meniscus) up to the fill line using a squirt bottle with distilled water.

STEP 4

After 1 minute, place the hydrometer bulb into the hydrometer flask and take your first hydrometer reading at two minutes. Readings should be taken at exactly 2, 5, 15, 30, and 60 minutes and at least 720 minutes (12 hours) and recorded on a sieve sheet. Record temperature from the control flask at the start of the test and at the end.

STANDARD OPERATING PROCEDURE
FOR
ASTM D422 - HYDROMETER ANALYSIS (Dry Method)
(continued)

STEP 5

After taking final reading; wash all soil/solution over the #200 sieve. Transfer the material retained on the #200 sieve into tare and place in the drying oven. After drying, pass the material over a nest of two sieves (#40 and #200 sieve). Weigh the material collected on each sieve and record on sieve sheet.

STEP 6

Check the data sheet for completeness.

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Approved by: Kirk Lowery 11/14/95

Geotechnical Laboratory Division
RUST Environment & Infrastructure

SOP Number: SOP-GT-07.2
Effective: July, 1995
Revision: 1

STANDARD OPERATING PROCEDURE FOR ASTM D422 - HYDROMETER ANALYSIS (Wet Method)

STEP 1

Complete all project information on the data sheet.

STEP 2

Collect approximately 200 grams of soil from the processed bulk. See SOP-GT-002, Step 6.1. Place the 200 gram sample into a marked plastic container; record container's ID on the worksheet and cover the soil in the plastic container with distilled and allow to soak or slake until soil will easily break down.

STEP 3

After soaking, use a wire wisp or spatula to thoroughly mix soil/water slurry. Pour slurry over a previously placed #10 sieve over a oven dried "Dog Bowl". Work the retained soil, as much as practical, through the sieve. Allow the minus #10 slurry in the "Dog Bowl" to dry to a thick paste. Record "Dog Bowl" number on worksheet in Hydrometer Section.

STEP 4

When a thick paste has developed, using a spatula cut four quarters into the soil paste. Remove opposite quarters and place into a pre-weight tare can for hygroscopic moisture content. Record tare can number, tare weight and wet weight of soil and tare on worksheet under hydro hydroscopic Moist. Content. Place into drying oven. Slice the two remaining quarter into halves. Remove opposite slices for hydrometer test. Place the removed slices into a tared or weighed glass beaker. Record soil weight and beaker ID on worksheet. Place 125 ml of hydro solution over the soil and allow to soak at least 16 hours.

STANDARD OPERATING PROCEDURE FOR ASTM D422 - HYDROMETER ANALYSIS (Wet Method) (continued)

STEP 5

After soaking, pour soil/solution mixture into the blender and mix for 1 minute. After 1 minute of mixing, transfer soil/solution mixture into hydrometer flask. Use a squirt bottle to remove all soil from the blender. Fill the hydrometer flask to just below the fill line with distilled water and the soil/solution mixture. Thoroughly mix the distilled water and soil/solution mixture by inverting and reversing the flask for 1 minute. Wash down any remaining soil on the sides of the flask and bring the water level (bottom of the meniscus) up to the fill line using a squirt bottle with distilled water.

STEP 6

After 1 minute, place the hydrometer bulb into the hydrometer flask and take your first hydrometer and temperature reading. Readings should be taken at exactly 2, 5, 15, 30, and 60 minutes and at least 720 minutes (12 hours) and recorded on a sieve sheet. Record temperature from the control flask at the start of the test and at the end.

STEP 7

After taking final reading; wash all soil/solution over the #200 sieve. Transfer the material retained on the #200 sieve into tare and place in the drying oven. After drying, pass the material over a nest of two sieves (#40 and #200 sieve). Weigh the material collected on each sieve and record on sieve sheet.

STEP 8

Check the data sheet for completeness.

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Designation: D 4972 – 89

Standard Test Method for pH of Soils[1]

This standard is issued under the fixed designation D 4972; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of the pH of soils for uses other than for corrosion testing. Such measurements are used in the agricultural, environmental, and the natural resources fields. This measurement determines the degree of acidity or alkalinity in soil materials suspended in water and a 0.01 *M* calcium chloride solution. Measurement in both liquids are necessary to fully define the soil's pH. This variable is useful in determining the solubility of soil minerals, the mobility of ions in the soil, and assessing the viability of the soil-plant environment. A more detailed discussion of the usefulness of this parameter is not warranted here, however, it can be found in many discussions of the subject. A few such discussions are given as Refs (1)[2] through (6) at the end of the text.

1.2 The values given in SI units are regarded as standard.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish ap[illegible]iate safety and health practices and determine the app[illegible]ability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 670 Practice for Preparing Precision and Bias Statements for Test Methods of Construction Materials[3]

G 51 Test Method for pH of Soil for Use in Corrosion Testing[4]

3. Summary of Test Method

3.1 Measurement of the pH of soils in both suspensions of water and a calcium chloride solution are made with either a potentiometer using a pH sensitive electrode system (Method A), or pH sensitive paper (Method B). The potentiometer is calibrated with buffer solutions of known pH. The pH sensitive paper is a less accurate measurement and should only be used for a rough estimate of the soil pH. The electrode must be used for this measurement unless the pH sensitive paper is specified.

4. Significance and Use

4.1 The pH of the soil is a useful variable in determining the solubility of soil minerals, the mobility of ions in the soil, and assessing the viability of the soil-plant environment.

4.2 pH measurements are made in both water and a calcium chloride solution, because the calcium displaces some of the exchangeable aluminum. The low ionic strength counters the dilution effect on the exchange equilibrium by setting the salt concentration of the solution closer to that expected in the soil solution. The pH values obtained in the solution of calcium chloride are slightly lower than those measured in water due to the release of more aluminum ions which then hydrolyses. Therefore, both measurements are required to fully define the character of the soil's pH.

4.3 For the purpose of this test method the test soil must be sieved through a No. 10 sieve (2 mm sieve mesh openings). Measurements on soils or soil fractions having particle sizes larger than 2 mm by this test method may be invalid. If soil or soil fractions with particles larger than 2 mm are used, it must be stated in the report since the results may be significantly different.

4.4 All water used for this test method must be distilled and deionized.

5. Interferences

5.1 This test method as measured by a pH probe has possible interferences due to a suspension effect or sedimentation potential. Users interested in a detailed discussion of the mechanism of this effect can find it in Refs (5) and (6).

5.2 This effect is the main reason Test Method G 51 can not be used for general measurement of pH outside of that for corrosion analysis. Test Method G 51 measures pH (an aqueous parameter) without adding any aqueous phase to the soil. This results in excessive soil particle-pH probe contact that over-estimates the activity of the hydrogen ions in solution and is therefore unacceptable for general soil analysis.

5.3 The suspension effect can be mitigated by careful attention to 9.1.

6. Apparatus

6.1 *Method A, pH Meter*—Potentiometer equipped with glass-calomel electrode system. Follow the manufacturer's instructions for the pH meter used. A silver/silver chloride electrode system or similar is also acceptable.

6.2 *Method B, pH Paper*—pH paper sensitive to a pH range from 1 to 12, with resolution to the nearest 0.2 pH unit.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents should conform to the specifications of the

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[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.22 on Soil as a Medi[illegible] Plant Growth.

Cu[illegible] edition approved Nov. 10, 1989. Published December 1989.

[2] The boldface numbers in parentheses refer to a list of references at the end of the test method.

[3] *Annual Book of ASTM Standards*, Vol 04.01.

[4] *Annual Book of ASTM Standards*, Vol 03.02.

Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Water should be distilled, deionized water, but not necessarily free of carbon dioxide. The pH of the water should be checked prior to testing the soil. Should it fall outside the range of 6.5 to 7.5, it should be discarded and other water obtained for the test.

7.3 *Acid Potassium Phthalate Buffer Solution* (0.05 *M*)—Dissolve 10.21 g (dried 1 h at 105°C) of potassium phthalate in water and dilute to 1 L. The pH of this solution should be 4.0 at 20°C. Protect the solution against evaporation and against contamination with molds. Replace the solution when mold is noticed. The effect of temperature is:

°C	pH
5 to 37	4.0

This illustrates that the pH of the solution does not change over the range in temperature from 5 to 37°C.

7.4 *Calcium Chloride Stock Solution* (1.0 *M*)—Dissolve 147 g of $CaCl_2 \cdot 2H_2O$ in water in a 1-L volumetric flask, cool, dilute to volume with water, and mix. Dilute 15 mL of this solution to 200 mL with water in a volumetric flask.

7.5 *Calcium Chloride Solution* (0.01 *M*)—Dilute 20.0 mL of stock 1.0 *M* $CaCl_2$ solution to 2 L with water. The pH of this solution should be between 5 and 7.

7.6 *Phosphate Buffer Solution* (0.025 *M*)—Dissolve 3.40 g of KH_2PO_4 and 3.55 g of Na_2HPO_4 in water and dilute to 1 L. Dry salts 2 h at 130°C before use. The pH of this solution should be 6.9 at 20°C. The effect of temperature is as follows:

°C	pH
0	7.0
10	6.9
20	6.9
30	6.8
40	6.8

8. Calibration of pH Meter

8.1 Calibrate the pH meter using the acid potassium phthalate and phosphate buffer solutions. Adjustment of the pH meter should follow the manufacturers direction.

9. Procedure

9.1 When making measurements with the pH electrode, place the electrode into the partially settled suspension to mitigate the suspension effect.

9.2 For both methods, begin with an air dried soil that has been sieved through a No. 10 sieve (2 mm holes) to remove the coarser soil fraction. Air drying the soil is necessary to accomplish sieving and to control the amount of water present at the time of measurement.

9.3 *pH in Distilled Water*—For both methods, weigh out approximately 10 g of air dried soil. Place the soil into a glass container and add approximately 10 mL of distilled water. Mix thoroughly and let stand for 1 h.

9.4 *Method A*—Read pH on pH meter.

9.5 *Method B*—Read pH on pH paper.

9.6 *pH in 0.01 M Calcium Chloride Solution*—For both methods weigh out approximately 10 g of air dried soil. Place the soil into a glass container and add approximately 10 mL of the 0.01 *M* $CaCl_2$ solution. Mix thoroughly and let stand for 1 h.

9.7 *Method A*—Read pH on pH meter.

9.8 *Method B*—Read pH on pH paper.

9.9 The mixture should be at approximately room temperature (15 to 25°C) at the time of pH measurement.

10. Report

10.1 Report the pH of the soil to the first decimal place. Specify which of the pH measurements is in water and which is in the calcium chloride solution. Also specify whether the determinations were made with Method A or Method B. If size fractions other than sieved through the No. 10 sieve are used, it must be stated in the report since the results may be significantly different.

11. Precision and Bias

11.1 *Precision:*

11.1.1 *Within-Laboratory Precision*—The within laboratory standard deviations for Method A are 0.031 (pH units) for the water mixture and 0.139[6] (pH units) for the calcium chloride mixture. Therefore, results of two properly conducted tests in the same or different laboratories should not differ by more than 0.065[6] (pH units) for the water mixture and 0.389 pH units for the calcium chloride mixture. The within-laboratory standard deviations for Method B are 0.189 (pH units) for the water mixture and 0.212[6] (pH units) for the calcium chloride mixture. Therefore, results of two properly conducted tests in the same or different laboratories should not differ by more than 0.53[6] (pH units) for the water mixture and 0.60 pH units for the calcium chloride mixture.

11.1.1.1 The precision of Method A presented was determined by the National Technical Center of the United States Department of Agriculture. In their evaluation they used 174 replicates for the water mixture and 32 replicates in testing the calcium chloride mixture.

11.1.1.2 The precision of Method B presented was determined by the United States Army Environmental Hygiene Agency. In their evaluation they used 25 replicates in testing each mixture.

11.1.2 *Between-Laboratory Precision*—The between-laboratory standard deviation has not been determined for either method. Subcommittee D18.06 is actively seeking data to evaluate the between laboratory precision of this test method.

11.2 *Bias*—There is no accepted reference value for this test method; therefore, bias cannot be determined.

12. Keywords

12.1 soil; pH; acidity; alkalinity; reaction

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the United States Pharmacopeia.

[6] These data satisfy the 1S and D2S requirements outlined in Practice C 670.

REFERENCES

(1) Garrels, R. M., and Christ, C. L., *Solutions, Minerals, and Equilibria,*" Freeman Cooper, San Francisco, CA, 1965.

(2) Greenland, D. J., and Hayes, M. H. B., *The Chemistry of Soil Processes,* Wiley, NY, 1981.

(3) Sposito, G., *The Thermodynamics of Soil Solutions,* Clarendon, Oxford, 1981.

(4) Davies, J. T., and Rideal, E. K., *Interfacial Phenomena,* Academic, NY, 1963.

(5) Hunter, R. J., *Zeta Potential in Colloid Science,* Academic, NY, 1981.

(6) Perrin, D. D., and Dempsey, B., *Buffers for pH and Metal Ion Control,* Chapman and Hall, London, 1974.

Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils[1]

This standard is issued under the fixed designation D 2974; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

. Scope

1.1 These test methods cover the measurement of mois- ıre content, ash content, and organic matter in peats and ıher organic soils, such as organic clays, silts, and mucks.

1.2 The values stated in SI units are to be regarded as the andard.

1.3 *This standard may involve hazardous materials, oper- ions, and equipment. This standard does not purport to ldress all of the safety problems associated with its use. It is e responsibility of the user of this standard to establish propriate safety and health practices and determine the olicability of regulatory limitations prior to use.*

Summary of Methods

2.1 *Method A*—Moisture is determined by drying a peat organic soil sample at 105°C. The moisture content is ɔressed either as a percent of the oven dry mass or of the 'eceived mass.

.2 *od B*—This is an alternative moisture method ːch removes the total moisture in two steps: (*1*) evapora- ı of moisture in air at room temperature (air-drying), and the subsequent oven drying of the air-dried sample at °C. This method provides a more stable sample, the dried sample, when tests for nitrogen, pH, cation ex- ıge, and the like are to be made.

3 *Methods C and D*—Ash content of a peat or organic sample is determined by igniting the oven-dried sample ı the moisture content determination in a muffle furnace 40°C (Method C) or 750°C (Method D). The substance ıining after ignition is the ash. The ash content is ex- sed as a percentage of the mass of the oven-dried sample.

4 Organic matter is determined by subtracting percent content from one hundred.

pparatus

Oven, capable of being regulated to a constant temper- of 105 ± 5°C.

TE—The temperature of 105°C is quite critical for organic soils. ven should be checked for "hot spots" to avoid possible ignition of ːcimen.

Muffle Furnace, capable of producing constant tem- ıres of 440°C and 750°C.

3.3 *Evaporating Dishes*, of high silica or porcelain of not less than 100-mL capacity.

3.4 *Blender*, high-speed.

3.5 *Aluminum Foil*, heavy-duty.

3.6 *Porcelain Pan, Spoons*, and equipment of the like.

3.7 *Desiccator.*

4. Preparation of Sample

4.1 Place a representative field sample on a square rubber sheet, oil cloth, or equivalent material. Reduce the sample to the quantity required by quartering and place in a moisture-proof container. Work rapidly to prevent moisture loss or perform the operation in a room with a high humidity.

MOISTURE CONTENT

5. Method A

5.1 Record to the nearest 0.01 g the mass of a high silica or porcelain evaporating dish fitted with a heavy-duty aluminum foil cover. The dish shall have a capacity of not less than 100 mL.

5.2 Mix thoroughly the representative sample and place a test specimen of at least 50 g in the container described in 5.1. Crush soft lumps with a spoon or spatula. The thickness of peat in the container should not exceed 3 cm.

5.3 Cover immediately with the aluminum foil cover and record the mass to the nearest 0.01 g.

5.4 Dry uncovered for at least 16 h at 105°C or until there is no change in mass of the sample after further drying periods in excess of 1 h. Remove from the oven, cover tightly, cool in a desiccator, and record the mass.

6. Method A Calculation

6.1 Calculate the moisture content as follows:

$$\text{Moisture Content, } \% = [(A - B) \times 100]/A$$

where:

A = mass of the as-received test specimen, g, and
B = mass of the oven-dried specimen, g.

6.1.1 This calculation is used primarily for agriculture, forestry, energy, and horticultural purposes and the result should be referred to as the moisture content as a percentage of as-received or total mass.

6.2 An alternative calculation is as follows:

$$\text{Moisture Content, } \% = [(A - B) \times 100]/B$$

where:

A = as-received test specimen, g, and
B = mass of the oven-dried specimen, g.

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[1] ɛse te‿ ‿thods are under the jurisdiction of ASTM Committee D-18 on Rock and are the direct responsibility of Subcommittee D18.18 on Peats ıted Materials.

ʼnt edition approved May 29, 1987. Published July 1987. Originally ʼd as D 2974 – 71. Last previous edition D 2974 – 84.

6.2.1 This calculation is used primarily for geotechnical purposes and the result should be referred to as the moisture content as a percentage of oven-dried mass.

Take care to indicate the calculation method used.

7. Method B

7.1 This method should be used if pH, nitrogen content, cation exchange capacity, and the like are to be tested.

7.2 Mix the sample thoroughly and select a 100 to 300 g representative sample. Determine the mass of this sample and spread evenly on a large flat pan. Crush soft lumps with a spoon or spatula and let the sample come to moisture equilibrium with room air. This will require at least 24 h. Stir occasionally to maintain maximum air exposure of the entire sample. When the mass of the sample reaches a constant value, calculate the moisture removed during air drying as a percentage of the as-received mass.

7.3 Grind a representative portion of the air-dried sample for 1 to 2 min in a high-speed blender. Use the ground portion for moisture, ash, nitrogen, cation exchange capacity tests, and the like.

7.4 Thoroughly mix the air-dried, ground sample. Weigh to the nearest 0.01 g the equivalent of 50 g of test specimen on an as-received basis. Determine the amount, in grams, of air-dried sample equivalent to 50 g of as-received sample, as follows:

$$\text{Equivalent Sample Mass, g} = 50.0 - [(50 \times M)/100]$$

where:

M = moisture removed in air drying, %.

Place the sample in a container as described in 5.1 and proceed as in Method A.

8. Method B Calculation

8.1 Calculate the moisture content as follows:

$$\text{Moisture Content, \%} = (50 - B) \times 2$$

where:

B = oven-dried sample, g.

8.1.1 This calculation gives moisture content as a percentage of as-received mass.

8.2 An alternative calculation is as follows:

$$\text{Moisture Content, \%} = [(50 - B) \times 100]/B$$

8.2.1 This calculation gives moisture content as a percentage of oven-dried mass.

ASH CONTENT

9. Method C

9.1 Determine the mass of a covered high-silica or porcelain dish.

9.2 Place a part of or all of the oven-dried test specimen from a moisture determination in the dish and determine the mass of the dish and specimen.

9.3 Remove the cover and place the dish in a muffle ace. Gradually bring the temperature in the furnace to C and hold until the specimen is completely ashed (no change of mass occurs after a further period of heating).

9.4 Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass.

9.5 This method should be used for all geotechnical and general classification purposes.

10. Method D

10.1 Determine the mass of a covered high-silica or porcelain dish.

10.2 Place a part of or all of the oven-dried test specimen from a moisture determination in the dish and determine the mass of the dish and specimen.

10.3 Remove the cover and place the dish in a muffle furnace. Gradually bring the temperature in the furnace to 750°C and hold until the specimen is completely ashed (no change of mass occurs after a further period of heating).

10.4 Cover with the retained aluminum foil cover, cool in a desiccator, and determine the mass.

10.5 This method should be used when peats are being evaluated for use as a fuel.

11. Calculation for Methods C and D

11.1 Calculate the ash content as follows:

$$\text{Ash Content, \%} = (C \times 100)/B$$

where:

C = ash, g, and

B = oven-dried test specimen, g.

ORGANIC MATTER

12. Calculation

12.1 Determine the amount of organic matter by difference, as follows:

$$\text{Organic matter, \%} = 100.0 - D$$

where:

D = ash content, %.

13. Report

13.1 Report the following information:

13.1.1 Results for organic matter and ash content, to the nearest 0.1 %.

13.1.2 Furnace temperature used for ash content determinations.

13.1.3 Whether moisture contents are by proportion of as-received mass or oven-dried mass.

13.1.3.1 Express results for moisture content as a percentage of as-received mass to the nearest 0.1 %.

13.1.3.2 Express results for moisture content as a percentage of oven-dried mass as follows:

(*a*) Below 100 % to the nearest 1 %.

(*b*) Between 100 % and 500 % to the nearest 5 %.

(*c*) Between 500 % and 1000 % to the nearest 10 %.

(*d*) Above 1000 % to the nearest 20 %.

14. Precision and Bias

14.1 The precision and bias of these test methods have not been determined. Data are being sought for use in developing a precision and bias statement.

STANDARD OPERATING PROCEDURE (SOP)

1. **TITLE**-Data Validation Procedures for EPA Level III Data

2. **PRINCIPLE REFERENCE**-

   U.S. EPA "National Functional Guidelines for Organic Data Review", December 1990, revised June, 1991.

   U.S. EPA "Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analysis", October 1989.

   U.S. EPA "Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses", July 1, 1988.

3. **APPLICATION**-The purpose of this Standard Operating Procedure (SOP) is to establish a uniform procedure for evaluating the quality of data obtained from laboratories. The validation procedures contained in this SOP are applicable to data where a summary Quality Control (QC) package has been required. Data may be validated against criteria in SW846, EPA 600 Series Methods, CLP, or other reference methods. The contents of the QC package can be determined by the client or specified in the Quality Assurance Project Plan (QAPP) or Sampling Analysis Plan (SAP), however, the following quality control results are generally reviewed:

<u>Organics</u>	<u>Inorganics</u>
Holding Times	Holding Times
Laboratory Blanks	Laboratory Blanks
Surrogate Spikes	Laboratory Duplicates
Matrix Spike/Matrix Spike Duplicates (MS/MSDs)	Laboratory Control Samples
Field Blanks	Matrix Spikes
Field Duplicates	Field Blanks
	Field Duplicates

Additional quality control results will be reviewed if required by the project. These include:

<u>Organics</u>	<u>Inorganics</u>
Tuning Results	Initial/Continuing Calibrations
Initial and Continuing Calibrations	ICP Serial Dilution
Internal Standard Areas	Post Digestion Spikes (PDS)
	Method of Standard Additions (MSA)

Note: This SOP is written mainly for water matrix samples, and limits may vary slightly for other matrices.

4. **SUMMARY OF PROCEDURE** - The goal of data validation is to document noncompliance to the QAPP/SAP or method criteria and to determine the affects of noncompliance on data usability/project objectives. During validation, qualifiers are placed on the data to identify quality control deviations as defined below; the following definitions are brief explanations of the validation qualifiers.

U - The analyte was analyzed for, but not detected above the reported quantitation limit.

J - The analyte was positively identified; the associated numerical value is the estimated concentration of the analyte in the sample.

UJ - The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

General Guidelines:

During the validation process it is important to document noncompliances to the method and/or QAPP/SAP (and samples affected) to ensure incorporation of these noncompliances into the validation report. A form has been included in Attachment 1 which may be useful to cite problems with data packages and indicate which QC parameters were evaluated.

Data qualifiers should be written directly on the analytical reports during validation. The reason for the qualifiers should be stated at the bottom of the sheet. Any changes to the qualifiers should be crossed out with a single line, initialized and dated. A red pen should be used for applying codes.

The QAPP/SAP and the field forms are tools for the validation process. The QAPP/SAP defines specific quality control limits required for the project and other pertinent information (completeness criteria for project). The field forms are necessary to identify field quality control samples since these samples are often blind to the lab and may be blind to the data reviewer.

5. **PROCEDURE-**

A. Completeness Evaluation

Assure that the following information is included in the data package, for each analyte and for each sample, as applicable. If this information is not available, contact the laboratory and obtain the missing data.

1. Chain-of-Custody Form

2. Cooler Receipt Form

3. Analytical results for each requested sample and analyte - the results received should be backchecked against the custody form to assure all requested analyses have been received.

4. QC data should also undergo a completeness check; the requested quality control data should be present for each sample.

5. Any reanalysis results due to out-of-control surrogates or internal standards (if reported).

6. Date of Analysis.

7. Date of Extraction (where applicable).

8. Method of Analysis.

9. Contract Required Quantitation Limits for aqueous samples should meet those which were requested (in QAPP/SAP); if not, verify that the sample was diluted. Detection limits achieved may not always be those requested for soil samples due to moisture content.

10. Batch number - Each sample for each type of analysis should be associated with a batch number so that the correct laboratory QC can be associated with it.

B. Organic Data Validation

The following guidelines are applicable to all organic analyses. When analyses are non-routine the reviewer should be thoroughly familiar with QAPP/SAP and method requirements.

1. Holding Times/Preservatives

Holding times are determined from the date of the samples collection to the date of analysis (or extraction).

a. Evaluate chain-of-custodies to determine sample collection date and the analytical report for the analysis and extraction dates. Chain-of-custodies should also be evaluated for correct preservation. Samples submitted for Volatile Organic Compounds (VOCs) should be preserved with 1:1 hydrochloric acid to a pH <2. At this time, it is also convenient to check that a trip blank is present in the specified frequency for aqueous VOCs.

b. The following table summarizes holding time requirements. For non-routine organics the QAPP/SAP should be reviewed for the correct holding time.

PARAMETERS	AQUEOUS	SOLIDS
Volatiles	14 days if preserved, 7 days if not preserved	14 days
Semivolatiles	Extraction - 7 days Analysis - 40 days from extraction	Extraction -14 days Analysis - 40 days from extraction
PCB/Pesticides	Extraction - 7 days Analysis - 40 days from extraction	Extraction -14 days Analysis - 40 days from extraction

c. All results for samples with holding time exceedances are qualified . If the holding time exceedance is minor (ie. within twice the holding time), results are qualified as estimated for nondetects and positive results (UJ and J, respectively). Samples exceeding twice the holding time (excessive holding time exceedance) are qualified as rejected (R) for nondetects and estimated (J) if a positive result. Samples exceeding holding time requirements are considered to have a potential for low bias due to constituent degradation during the prolonged holding times.

1. If aqueous VOCs were not preserved this should be noted in the validation report and holding time qualifications are based on 7 days.

2. If a trip blank is not present in the specified frequency for aqueous VOCs, this should be stated in the validation report and associated samples listed.

d. Sample temperature on arrival at the laboratory should be 4°C±2°C. Samples arriving at temperature outside this range should be qualified as follows:

VOCs

- Intact samples between 2-6°C. No qualifiers.
- Samples between 6-10°C. All results qualified as estimated (UJ and J).
- Samples greater than 10°C. All nondetect results qualified R. Positive results qualified J.

BNAs, PCB/Pesticides and Herbicides

- Intact samples between 2-6°C. No qualifiers.
- Samples greater than 6°C. All results qualified as estimated (UH and J).

2. GC/MS Tuning

Results of GC/MS tunes (often reported on CLP form V) should be reviewed to insure that ion abundance criteria as stated in the method of analysis is achieved. If criteria has not been met, contact the lab to verify that a transcription error has not been made (request raw data). If critical ion abundance criteria as defined below are not met, both non detect results and positive results should be rejected (R). If relative abundances of non-critical ions are outside criteria, nondetects and positive results should be qualified as estimated (UJ and J, respectively).

BFB:

Characteristics Ions
50
75
95/96
174/175
174/176
176/177
173

DFTPP:

Critical Ions	Non-critical Ions
198/199	51
442/443	127
68	275
70	
197	
441	
365	

Tune forms should also be reviewed to verify samples were analyzed within the 12 hour tune period. The 12 hour tune period starts at the injection time of the tuning compound (BFB or DFTPP). All subsequent sample injections should be within this twelve hour time frame. If exceedances are evident (usually minor) note these in the validation report. If the reviewer has reason to believe the exceedance of the 12 hour tune period has affected data quality/usability; results should be qualified.

3. **Calibration**

a. Initial Calibration

The initial calibration curve for volatile and semivolatile analyses must contain five calibration points, include all compounds reported and reflect the linear range of the instrument. The percent Relative Standard Deviation (%RSD) and Relative Response Factors (RRFs) for each compound must be reported.

1. %RSDs must be ≤30% for CCC compounds (VOA and SVOA). Positive results associated with the CCC compounds exceeding this limit should be qualified (J). Nondetects associated with high %RSDs should also be qualified (UJ) if the exceedance is excessive (ie.,>50%RSD).

2. If an SPCC has any initial calibration RRF which is <0.05 for SVOA or <0.3 for VOA, except bromoform, <0.25, qualify positive results for this compound as estimated (J) and nondetects as rejected (R) in associated samples.

The initial calibration curve for GC analyses (PCB/pesticides, herbicides) require five calibration points for single component compounds and three calibration points for multi-component compounds (ie aroclors, toxaphene & chlordane), must include all compounds reported (including surrogates), and reflect the linear range of the instrument. The percent Relative Standard Deviation (%RSD) for each compound must be reported. If the %RSD criteria is not met (20% for single component and 30% RSD for multi-components), qualify associated positive results as estimated (J). If the exceedance is excessive (>40%RSD), qualify both positive and nondetects (J and UJ, respectively) per SW-846.

b. Continuing Calibration

The continuing calibration standards for volatile and semivolatile analyses must be analyzed at the start of each 12 hour analysis period and must include all compounds reported including surrogates. The Percent Difference (%D) and the Relative Response Factor (RRF) for each compound must be reported.

1. %Ds must be ≤25% for VOA CCC compounds or ≤30% for SVOA CCC compounds. Positive results associated with CCC compounds exceeding this limit should be qualified J. Nondetects associated with high %Ds should also be qualified (UJ) if the exceedance is excessive (ie., >50%D).

2. If an SPCC compound has a continuing calibration RRF which is less than 0.05 (SVOA) or 0.3 (VOA; except bromoform, 0.25), quality positive results for this compound as estimated (J) and nondetects as rejected (R) in associated samples.

Continuing calibration checks for GC analyses (PCB/Pesticides, herbicides) are to be analyzed every ten analyses and must include all single component Pesticides reported (including surrogates). If the %D reported is greater than 15%, associated positive results should be qualified as estimated (J). Nondetects associated with high %D should also be qualified (UJ) if the exceedance is excessive (ie.,>30%D).

4. Blanks

The purpose of the laboratory blanks (or field blanks) is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The procedure for evaluating blanks applies to all types of blanks (ie., method blanks, instrument blanks, trip blanks, and field blanks); however, there is an order (or hierarchy) in which they should be evaluated (ie. method/instrument blanks, trip blanks, and lastly field blanks). Results must <u>not</u> be corrected by subtracting any blank values.

Frequency - The frequency of blanks should be as stated in the QAPP/SAP or method (usually daily or every 20 samples) and blanks should be submitted for every matrix analyzed. If the frequency criteria has not been met, this should be stated in the validation report.

a. Laboratory Blanks - The B qualifier used by the laboratory should be eliminated and a U qualifier applied as discussed below. If a compound is found in the blank but not the associated samples, no action is taken.

Common Lab Contaminants:

Volatiles	Semivolatiles
Methylene Chloride	Phthalates
Acetone	
2-Butanone	
Toluene	

The 10Xs rule applies to common lab contaminants: A compound detected in the sample and also detected in the blank is qualified U if the sample concentration is less than 10Xs the blank concentration. The quantitation limit should also be evaluated:

If the reported value is less than the quantitation limit, this value should be raised to the quantitation limit and qualified U. Example (using 10Xs rule):

Blank result	7
Quantitation limit	5
Sample result	3J
Validated result	5U

If the reported value is greater than the quantitation limit, the value should remain as reported and qualified U. Example (using 10Xs rule):

Blank result	7
Quantitation limit	5
Sample result	50
Validated result	50U

Data users should be made aware of elevated detection limits due to blank contamination in the validaton report. The 5Xs rule follows the same procedure; however, it applies to target compounds which are not common lab contaminants.

b. Trip Blanks (VOCs) - If trip blanks show contamination that is not related to the lab, associated samples should be qualified using the 5Xs rule.

c. Rinsate Blanks - In general, results for rinsate blanks are only applicable to aqueous samples. Positive results in the rinsate blank, that are not related to the lab or shipment (trip blank) are considered to be contamination from inadequate field decontamination procedures. Associated field samples should be qualified using the procedure discussed above (5Xs rule).

5. Surrogate Spike

Surrogate recoveries should be evaluated using limits as specified in the QAPP/SAP. Every sample should have surrogate recovery results if required in the method.

a. High recovery: Qualify positive results J; a high bias is present. Non detects are unaffected.

b. Low recovery (but greater than 10%): Qualify both nondetects (UJ) and positive results (J); a low bias is present.

c. Very low recoveries (less than 10%): Qualify positive results as J and nondetects as R.

d. Both a low recovery and high recovery are present: Qualify as in (b) unless a recovery is less than 10%; use (c) in this case.

When evaluating semivolatiles, 2 surrogate recoveries need to be out-of-control in the same fraction (ie. 2 acids or 2 base/neutrals) and only compounds of the out-of-control fraction are qualified as in (a) and (b) from above. If any one surrogate recovery for semivolatiles is less than 10%, the associated fraction is qualified as in (c).

If surrogate recoveries are outside the established limits for VOCs, a reanalysis may be required; refer to the QAPP/SAP to confirm if this requirement exists. If the reanalysis results are within the surrogate limits, only the reanalysis results should be reported. If both analyses are outside surrogate limits, the results associated with the sample producing surrogate recoveries closer to the established limits should be used.

6. Matrix Spikes/Matrix Spike Duplicates

Quality control limits as specified in the QAPP/SAP should be used to evaluate MS/MSD recoveries. RPD's are reported for all organics, but the limits are not applicable per SW-846. Generally, only the unspiked sample is qualified if the MS/MSD is outside established limits.

a. High recovery: Qualify the compound exhibiting the high recovery J in the unspiked sample if the result is positive; a high bias is present. Nondetects are unaffected.

b. Low recovery (but greater than 10%); Qualify both nondetects and positive results (UJ and J, respectively) for only the compound which exhibited the low recovery in the unspiked sample; a low bias is present.

c. Very low recoveries (less than 10%): Qualify the compound exhibiting the very low recovery J if the result of this compound in the unspiked sample is positive and R if nondetected.

d. Both a low recovery and high recovery are present: Qualify as in (b) unless a recovery is less than 10%; use (c) in this case.

7. Laboratory Control Samples

Qualify samples based on limits as presented in the QAPP/SAP. If limits are not presented in the QAPP/SAP, use limits submitted by the laboratory. Quality recoveries as in 6 a-d.

8. Internal Standard Areas

Internal standard area counts are evaluated for GC/MS analyses (volatiles and semivolatiles) to ensure that the sensitivity and response are stable during each analysis.

Internal standard area counts must not vary by more than a factor of two (-50% to +100%) from the associated calibration standard. If the area count for each sample or blank is outside - 50% or +100% of the area of the associated standard:

a. Positive results for compounds quantitated using that internal standard should be qualified J.

b. Nondetected compounds quantitated using an internal standard count greater than 100% should <u>not</u> be qualified.

c. Nondetected compounds quantitated using an internal standard count less than 50% are reported as the associated sample quantitation limit and qualified as UJ.

d. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. A severe loss of sensitivity is defined as an area count less than 25% of the lower limit or less than a 5000 area count. Nondetected target compounds should then be qualified as unusable (R). Positive results should be qualified as estimated (J).

Internal standard retention times: If the internal standard retention time varies more than 30 seconds, the data must be re-evaluated by the lab and raw data submitted for data review.

9. Confirmation

Positive results need to be confirmed via a second chromatography column for analyses performed via GC or LC analyses (not required for GC/MS analyses). The parameters which specifically require second column confirmation are PCB/pesticides. For positive results, verify that the results were confirmed. If the positive results were not confirmed, qualify the result as estimated (J).

10. Field Duplicates

The Relative Percent Difference (RPD) should be calculated for positive results and results presented in table format with the validation report. If one of the values is a nondetect, the quantitation limit should be used to calculate the RPD.

Qualifiers are generally not assigned based on high RPDs; however, if field duplicates do not agree with QAPP/SAP requirements, it should be noted in the validation report.

C. Metals Data Validation

The following guidelines are applicable to all metals analyses. The reviewer should be thoroughly familiar with QAPP/SAP and method requirements. If a CLP reporting format is submitted, the B qualifier which indicates that the concentration is less than the Contract Required Detection Limit (CRDL) but greater than the instrument detection limit (IDL), should be removed to eliminate confusion as to what this qualifier means (it is often thought to be lab contamination).

1. Holding Times/Preservatives

Holding times are determined from the date of the sample collection to the date of analysis.

a. Evaluate chain-of-custodies to determine sample collection date and the analytical report for the analysis dates. Chain of custodies should also be evaluated for correct preservation. Aqueous metals samples should be preserved with 1:1 nitric acid to a pH <2 and aqueous cyanide samples preserved with sodium hydroxide to a pH>12.

b. The following table summarizes holding time requirements.

Parameters	Holding Times
Mercury	28 days
Other Metals	6 months
Cyanide	14 days

c. All results for samples with holding time exceedances are qualified. If the holding time exceedance is minor (ie. within twice the holding time) nondetects and positive results are qualified as estimated (UJ and J respectively). Samples exceeding twice the holding time (excessive holding time exceedance) are qualified as rejected (R) for nondetects and estimated (J) if a positive result.

1. If aqueous metals or cyanide are not preserved at the time of collection, qualify positive results and nondetects as estimated (UJ and J, respectively).

2. Sample temperature is not a concern for metals. Cyanide samples should be maintained at 4 ± 2°C. If cyanide samples were received at a temperature >6° C, qualify results of nondetects and positive results as estimated (UJ and J, respectively).

2. Calibration

A blank and at least 3 standards (4 standards for mercury) must be used in establishing the initial calibration curve. If not, qualify data as unusable (R). A mid-range standard must be distilled for cyanide. The correlation coefficient should be $\geq$0.995, if not qualify nondetects and positive results as estimated (UJ and J, respectively).

Initial and continuing calibration verification (ICV and CCV) control limits:

Metals (excluding mercury):	90-110% Recovery
Mercury:	80-120% Recovery
Cyanide:	85-115% Recovery

If the ICV or CCV % recoveries fall outside the acceptance windows within the ranges of:

Metals (excluding mercury):	75-89%
Mercury:	65-79%
Cyanide:	70-84%

Qualify both nondetects and positive results as estimated (UJ and J).

Metals (excluding mercury):	<75%
Mercury:	<65%
Cyanide:	<70%

Qualify both nondetects and positive results as unusable (R).

Metals (excluding mercury):	111-125%
Mercury:	121-135%
Cyanide:	116-130%

Qualify positive results as estimated (J). Nondetects are usable.

Metals (excluding mercury):	>125%
Mercury:	>130%
Cyanide:	>135%

Qualify positive results as unusable (R). Nondetects are usable (no qualifiers).

3. **Blanks**

The purpose of laboratory blanks (or field blanks) is to determine the existence and magnitude of contamination resulting from laboratory (or field) activities. The procedure for evaluating blanks applies to all types of blanks (ie. method blanks, instrument blanks, and field blanks); however, there is an order (or hierarchy) in which they should be evaluated (ie. first method/instrument blanks, and last field blanks).

Frequency - The frequency of blanks should be as stated in the QAPP/SAP or method (usually every 20 samples) and blanks should be submitted for every matrix analyzed. If the frequency criteria has not been met, this should be stated in the validation report.

a. Laboratory Blanks - If a metal is found in the blank but <u>not</u> the associated samples, no action is taken.

If the concentration of an analyte in the blank exceeds the CRDL (or reporting limits if CLP forms are not used) qualify associated positive results within five times the concentration of the blank as U. (See reference #3).

For analytes with negative results whose value exceeds - the CRDL (or reporting limit if CLP forms are not used), nondetects should be qualified as unusable (R). Positive results within 3X the CRDL should be qualified as estimated (J) and are considered to have a potential for low bias. Positive results greater than 3Xs the CRDL are acceptable.

b. Field Blanks - In general, results for field blanks are only applicable to water samples. If contamination that is not related to the lab is found, associated field samples should be qualified using the procedure discussed above.

4. Laboratory Control Samples (LCS)

Aqueous LCSs:

All results should be within 80-120% recovery or as defined in the QAPP/SAP.

If the recovery for a metal is low (50-79% recovery), qualify associated nondetects and positive results as estimated (UJ and J, respectively). The qualified results have a potential for low bias.

If the recovery for a metal is very low (<50%), qualify associated sample results as unusable (R).

If the recovery is high (>120%), do not qualify associated nondetects; qualify associated positive results as estimated (J). Positive results qualified have a potential for high bias.

5. Laboratory Duplicates

For sample results greater than 5Xs the CRDL (or reporting limit): duplicate results should be within 20 RPD. If not, qualify associated positive results as estimated (J).

If one or both sample results are less than 5Xs the CRDL: duplicate results should be within ± the CRDL. If not, qualify the associated positive results as estimated (J).

The direction of the sample bias cannot be determined due to laboratory duplicate imprecision.

6. Matrix Spikes

Spike recoveries must be within 75-125% recovery or as defined in QAPP/SAP, however, these limits do not apply when the concentration of the metal in the sample exceeds the concentration of the spike by a factor of 4 (this QC data cannot be used for qualifying samples).

If the recovery for a metal is low (30-74% recovery), qualify associated results as estimated (UJ and J). The qualified results have a potential for low bias.

If the recovery for a metal is very low (<30%), qualify associated positive results as estimated (J) and nondetects as unusable (R). Positive results have a potential for a low bias while nondetects are unusable - the presence or absence of this analyte cannot be verified.

If the recovery is very high (>120% recovery), do not qualify associated nondetects; qualify associated positive results as estimated (J). Positive results qualified have a potential for high bias.

7. Furnace QC

Post Digestion Spikes: Metals ran via furnace methodologies are required to run post digestion spikes (PDSs). Recovery limits for PDSs are 85-115% recovery.

a. If the recovery is ≥10% and <85% qualify both nondetects and positive results as estimated (UJ and J, respectively).

b. If the recovery is >115% qualify positive results as estimated (J).

c. If the recovery is <10% qualify positive results as estimated (J) and nondetects as unusable (R).

Method of Standard Additions (MSA): If it is evident that MSA is required but has not been performed, qualify nondetects and positive results as estimated (UJ and J, respectively). If the MSA correlation coefficient is <0.995, qualify nondetects and positive results as estimated (UJ and J, respectively).

8. ICP Serial Dilution

ICP metals with a sufficiently high sample concentration should be evaluated for chemical interferences due to matrix effects. Only metals with sample concentrations greater than 50 times the IDL should be evaluated. The original result and a five fold dilution must agree within 10% Difference (%D). If this criteria is not met, qualify associated sample results for that analyte as estimated (J) if the sample concentration is greater than 50 times the IDL.

9. Field Duplicates

Field Duplicates - The relative percent difference (RPD) should be calculated for positive results and results presented in table format with the validation report. If one of the values is a nondetect, the reporting limit should be used to calculate the RPD. If one or both of the results are less than five times the reporting limit, a control limit of +/- 2Xs will be used.

Qualifiers are generally not assigned based on high RPDs, however, if field duplicates do not agree with QAPP/SAP requirements, this should be discussed in the validation report.

6. DOCUMENTATION-

A validation report is required for all data validated and is submitted as a technical memorandum. It should include QC parameters which were evaluated and all noncompliances to the QAPP/SAP or analytical methods. If noncompliances affect data quality and validation codes are applied, the affected samples should be listed with a discussion regarding the affects of the noncompliance on the data included (ie. whether sample bias can be determined). An overall discussion is also necessary which states whether the data has met the objectives of the project (completeness evaluation), if resampling needs to occur (usually this is evident to the project chemist before the validation stage), and the effects of rejected data on the project.

A final comparison of codes reported in the validation report should be made to codes present on hardcopy reports. The reviewer should evaluate the validation report and the hardcopy results (and database results) to verify that codes discussed in the report are present on hard copies (and in the database).

7. **CALCULATIONS**-All calculations are per the WMX Environmental Monitoring Laboratories, Inc., Comprehensive Quality Assurance Plan (QAPP).

8. REFERENCES-

WMX Environmental Monitoring Laboratories, Inc., Comprehensive Quality Assurance Plan (QAPP), August 5, 1994.

U.S. EPA "Test Methods for Evaluating Solid Waste Physical/Chemical Methods", SW-846 3rd. Edition November, 1986, Final Update July, 1992.

Any method references cited in facility's permit, QAPP or SAP.

ATTACHMENT A

Level III Data Quality Review
Data Review Worksheets

Site Name________________________

REVIEW OF ORGANIC DATA PACKAGE

The hardcopied (laboratory name)____________________________data package has been reviewed and the quality assurance and performance data summarized. The data review included:

No. of Samples_________________
Matrix__________________________
VOCs, SVOCs, PCB/Pesticides

Sampling Date(s)________________
Shipping Date(s)________________
Date Received by Lab___________

Sample Nos:

Trip Blanks No.:

Rinsate Blank No.:

Field Dup. Nos:

The general criteria used to determine the performance were based on an examination of:

___Data Completeness
___Holding Times
___GC/MS Tuning
___Calibrations
___Lab Control Samples
___Laboratory and Field Blanks
___Surrogate Recoveries
___Mat.Spikes/Mat. Spike Duplicates
___Internal Standards
___Quantitation Limits
___Field Duplicate Precision

Overall Comments:

Reviewer:__________________________________ **Date:**_____________

Level III Data Quality Review
Data Review Worksheets

Site Name________________

I. DATA COMPLETENESS

MISSING INFORMATION	DATE LAB CONTACTED	DATE RECEIVED

Level III Data Quality Review
Data Review Worksheets

Site Name____________________

II. HOLDING TIMES

Complete table for all samples and circle the fractions which are not within the criteria.

SAMPLE ID	DATE SAMPLED	VOA DATE	BNA DATE EXTR	BNA DATE ANAL.	PEST DATE EXTR.	PEST DATE ANAL.

VOA Aqueous (unpreserved) - 7 days
Aqueous (preserved) - 14 days
BNA & PEST. Waters: Extract within 7 days, analyze within 40 days
ACTION: 1. If holding times are exceeded all positive results are estimated (J) and non-detects are estimated (UJ)

2. If holding times are grossly exceeded (2 weeks or greater) the reviewer may determine that nondetects are unusable (R).

Level III Data Quality Review
Data Review Worksheets

Site Name________________

III GC/MS TUNING

_____ The DFTPP performance results were reviewed and found to be within the specified criteria and samples analyzed within the 12 hour tune period.

If no,
Samples affected:________________________________

_____ The BFB performance results were reviewed and found to be within the specified criteria and samples analyzed within the 12 hour tune period.

If no,
Samples affected:________________________________

If mass calibration is in error to the validation guidelines for expanded criteria. If necessary, qualify all associated data as unusable (R).

Describe specific problems below:

Level III Data Quality Review
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Site Name______________________

IV. CALIBRATIONS

Fraction:________________ Dates of Initial Calibration:__________
Instrument ID:____________ Dates of Continuing Calibration_________

DATE	COMPOUNDS	EXCEEDANCES	SAMPLES QUALIFIED

1. Average RRF's and RRF's must be $\geq$0.05 (SVOC's, SPCC's) or $\geq$0.3 (VOC's, SPCC's except Bromoform $\geq$ 0.25).

2. %RSD's must be $\leq$30% (VOCs & SVOCs) for CCC compounds. %RSD's must be $\leq$20% for GC.

3. %D's must be $\leq$25% (VOC's) or $\leq$30% (SVOC's) for CCC compounds. %D's must be $\leq$ 15% (GC).

 Site Name____________________

V. LABORATORY CONTROL SAMPLE

List any recoveries not within the SAP/QAPP criteria and the sample affected.

Matrix____________________

DATE	LAB ID.	EXCEEDANCES	RESULTS QUALIFIED

Data Review Worksheets

VI. BLANK ANALYSIS RESULTS

List the contaminants in the blank below.

1. Laboratory Blanks

DATE	LAB ID	FRACTION/ MATRIX	COMPOUND DETECTED/ CONC.	SAMPLES QUALIFIED

2. Rinsate and Trip Blanks

DATE	FIELD ID.	FRACTION/ MATRIX	COMPOUND DETECTED/ CONC.	SAMPLES QUALIFIED

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VII. SURROGATE RECOVERIES

List the percent recoveries which do not meet the criteria for surrogate recovery.

Matrix__________

FIELD ID	VOA DCE	VOA TOL	VOA BFB	BN NZB	BN FBP	BN TPH	ACID PHL	ACID 2FP	ACID TBP	PCB/ PEST TCMX	PCB/ PEST DCP

Surrogate Actions:	PERCENT RECOVERY		
	<10%	<RRR	>RRR
Positive Sample Results	J	J	J
Non-detected Results	R	UJ	Acceptable

RRR=Required Recovery Range (SAP or QAPP)

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VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

1. Matrix Spike/Matrix Spike Duplicate Recoveries and Precision

List the samples spiked.

FRACTION	FIELD ID	LEVEL	MATRIX

List the percent recoveries and RPD's of compounds which do not meet the criteria in the SAP/QAPP. (Criteria not applicable to SW846 methods, RPDs reported only).

MS or MSD	COMPOUND	%REC/RPD	QC LIMITS

QUALIFICATION IS LIMITED TO THE UNSPIKED SAMPLE ONLY.

1. If any compound does not meet the Required Recovery Range (RRR) as specified in the SAP/QAPP follow the actions stated below.

	PERCENT RECOVERY		
	<10%	10%-RRR	> RRR
Positive Sample Results	J	J	J
Non-detected Results	R	UJ	Acceptable

Level III Data Quality Review Site Name__________________
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IX. INTERNAL STANDARD PERFORMANCE

List the internal standard areas of samples which do not meet the criteria of +100% or -50% of the internal standard area in the associated continuing calibration standard.

FIELD ID	DATE	IS OUT	IS AREA/RT	ACCEPTABLE RANGE	ACTION

ACTION:

1. If an IS area count is outside the criteria -50% or +100% of the associated standard:

a. Positive results for compounds quantitated using that IS are flagged as estimated (J) for that sample fraction.

b. Nondetects for compounds quantitated using that IS are flagged as estimated (UJ) for that sample fraction.

c. If extremely low area counts are reported, or if performace exhibits a major drop-off, then a severe loss of sensitivity is indicated. Nondetects should be flagged as unusable (R).

2. If an IS retention time varies more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exists. For shifts of a large magnitude, the reviewer may consider partial or total rejection of the data for that sample fraction.

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X. QUANTITATION

List samples/fraction which did not meet QAPP/SAP quantitation limits with an explanation.

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XI. FIELD DUPLICATE PRECISION

Sample Nos.________________ , ________________ Matrix:________________
List the concentrations and RPD of the compounds detected in the field duplicate. Circle RPDs that do not meet QAPP/SAP criteria.

FRACTION	COMPOUND	SAMPLE CONC.	FIELD DUP CONC.	RPD

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REVIEW OF INORGANIC DATA PACKAGE

The hardcopied (laboratory name) ______________________________ data package has been reviewed and the quality assurance and performance data summarized. The data review included:

No. of Samples__________ Sampling Date(s)________________

Matrix__________________ Shipping Date(s)________________

Date Rec'd by lab_______________

Sample Nos:

Rinsate Blank Nos:

Field Dup Nos.

The general criteria used to determine the performance were based on an examination of:

___Data Completeness
___Holding Times
___Calibrations
___Blanks
___Matrix Spike Recoveries
___Laboratory Duplicates
___Laboratory Control Samples
___Furnace AA Results
___ICP Serial Dilution Results
___ICP Interference Check
___Quantitation
___Field Duplicates

Overall comments:

Reviewer: __________________________________ **Date:** ____________________

Level III Data Quality Review
Data Review Worksheets

Site Name___________________

I. DATA COMPLETENESS

MISSING INFORMATION	DATE LAB CONTACTED	DATE RECEIVED

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II. HOLDING TIMES Complete table for all samples and circle the fractions which are not within the criteria.

SAMPLE ID.	DATE SAMPLED	Hg ANALYSIS DATE	CYANIDE ANALYSIS DATE	OTHERS ANALYSIS DATE	pH	ACTION

METALS 180 DAYS FROM SAMPLE COLLECTION
MERCURY 28 DAYS FROM SAMPLE COLLECTION
CYANIDE 14 DAYS FROM SAMPLE COLLECTION

ACTION:
1. If holding times are exceeded all positive results are estimated (J) and nondetects are estimated (UJ).

2. If holding times are grossly exceeded, the reviewer may determine that nondetects are unusable (R).

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III.A. CALIBRATIONS

1. Recovery Criteria

List the analytes which did not meet the percent recovery (%R) criteria for Initial or Continuing Calibration.

DATE	ICV/CCV#	ANALYTE	% R	ACTION	SAMPLES AFFECTED

ACTIONS:

If any analyte does not meet the %R criteria follow the actions stated below:

For Positive Results:

	ACCEPTED	ESTIMATED (J)	REJECTED (R)
METALS	90-110%R	75-89%R, 111-125%R	<75%R, >125%R
MERCURY	80-120%R	65-79%R, 121-135%R	<65%R, >135%R
CYANIDE	85-115%R	70-84%R, 116-130%R	<70%R, >130%R

For Nondetect Results:

	ACCEPTED	ESTIMATED (UJ)	REJECTED (R)
METALS	90-125%R	75-89%R	<75%R, >125%R
MERCURY	80-135%R	65-79%R	<65%R, >135%R
CYANIDE	85-130%R	70-84%R	<70%R, >130%R

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III B. CALIBRATIONS

2. Analytical Sequence

   A. Did the laboratory use the proper number of standards for calibration as described in the analytical method?
   YES or NO

   B. Were calibrations performed at the beginning of each analysis?
   YES or NO

   C. Were calibration standards analyzed at the beginning of sample analysis and at a minimum frequency of ten percent of every two hours during analysis, whichever is more frequent?
   YES or NO

   D. Were the correlation coefficients for the calibration curves for AA, Hg and CN $\geq$0.995?
   YES or NO

   E. Was a standard at 2xCRDL analyzed for all ICP analyses?
   YES or NO

If NO, the data may be affected. Use professional judgement to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

Level III Data Quality Review
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Site Name____________________

IV. BLANK ANALYSIS RESULTS

List the contaminants in the blanks below.

1. Laboratory Blanks

Matrix__________

DATE	ICB/CCB#	PREP BLANK	ANALYTE DETECTED/CONC.	SAMPLES QUALIFIED

2. Rinsate Blanks

DATE	FIELD ID	ANALYTE DETECTED	CONC.	SAMPLES QUALIFIED

3. Frequency Requirements

   A. Was a preparation blank analyzed for each matrix, for every 20 samples and for each digestion batch? YES or NO

   B. Was a calibration blank run every 10 samples or every 2 hours whichever is more frequent? YES or NO

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Data Review Worksheets

V. MATRIX SPIKE/MATRIX SPIKE DUPLICATE

1. Matrix Spike/Matrix Spike Duplicate Recoveries and Precision

Sample No.___________,__________ Level:_________ Matrix:_________

List the percent recoveries and RPD's of compounds which do not meet the criteria stated on Form 3.

MS or MSD	ANALYTE	%REC/RPD	QC LIMITS

Matrix Spike Actions apply to all samples of the same matrix.

ACTIONS:

1. If the sample concentration exceeds the spike concentration by a factor of 4 or more, no action is taken.
2. If any analyte does not meet the %R criteria, follow the actions below.

		PERCENT RECOVERY	
	<30%	30%-RRR	>RRR
Positive Sample Results	J	J	J
Nondetected Results	R	UJ	Acceptable

RRR=Required Recovery Range (QAPP or SAP)

2. Frequency Criteria

   A. Was a matrix spike prepared at the required frequency? YES or NO
   B. Was a post digestion spike analyzed for elements that did not meet required criteria for matrix spike recovery? YES or NO

Level III Data Quality Review
Data Review Worksheets

Site Name__________________

VI. LABORATORY DUPLICATES

List the concentrations of any analyte not meeting the criteria for laboratory duplicate precision. Indicate what criteria was used to evaluate precision by circling either the RPD or reporting limit for each element.

Matrix:_______________

ELEMENT	REPORTING LIMIT WATER	SAMPLE #	DUP. #	RPD	ACTION

Laboratory duplicate actions should be applied to all other samples of the same matrix.

ACTIONS:

1. Estimate (J) positive results for elements which have RPD greater than SAP (QAPP) limits.

2. If sample results are less than 5X the reporting limit, estimate (J) positive results for elements whose absolute difference is the reporting limit.

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VII. LABORATORY CONTROL SAMPLE

1. AQUEOUS LCS

List any LCS recoveries not within the 80-120% (or SAP/QAPP) criteria and the samples affected.

Matrix:_______________

DATE	ELEMENT	%REC	ACTION	SAMPLES AFFECTED

Level III Data Quality Review
Data Review Worksheets

Site Name____________________

VIII. FURNACE ATOMIC ABSORPTION ANALYSIS

1. Duplicate Precision

____________ Duplicate injections and one-point analytical spike were performed for all samples; duplicate injections agreed within ±20%.

____________ Duplicate injections and/or spikes were not performed for the following samples/elements:

____________ Duplicate injections did not agreed within ±20% for all samples/elements:

2. Post Digestion Spike Recoveries

____________ Spike recoveries met the 85-115% recovery criteria for all samples.

____________ Spike recoveries did not meet the 85-115% criteria, but did not require MSA for the following samples/elements:

____________ MSA was used to quantitate analytical results when required:

________ Correlation coefficients ≥0.995, accept results.

________ Correlation coefficients <0.995 for samples/elements:

____________ MSA was not performed as required for samples/elements:

ACTION:

1. Estimate (J) positive results if duplicate injections are outside ±20% RSD.

2. If the post digestion spike recovery was outside the required limits:

	Percent Recovery		
	<10%	11%-84%	>115%
Positive Results	J or R	J	J
Nondetected Results	R	UJ	Acceptable

3. Estimate (J) sample results if the MSA was required and not performed.

4. Estimate (J) sample results if coefficient was <0.995.

Level III Data Quality Review   Site Name____________________
Data Review Worksheets

IX. ICP SERIAL DILUTIONS

_____________ Serial Dilutions were performed for each matrix and results of the diluted sample analysis agreed within 10% of the original undiluted analysis.

_____________ Serial Dilutions were not performed for the following:

_____________ Serial Dilutions were performed, but analytical results did not agree within 10% for analyte concentrations greater than 50X the IDL before dilution.

Matrix__________

ELEMENT	IDL	50xIDL	SAMPLE RESULT	SERIAL DILUTION	%D	ACTION
Aluminum						
Barium						
Beryllium						
Cadium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Nickel						
Potassium						
Silver						
Vanadium						
Zinc						

Actions apply to all samples of the same matrix.

ACTIONS:
1. Estimated (J) positive results if %D >15.

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Site Name__________________

X. ICP INTERFERENCE CHECK SAMPLE

1. Recovery Criteria

List any element in the ICS AB solution which did not meet the criteria for % recovery.

DATE	ELEMENT	%R	ACTION	SAMPLES AFFECTED

ACTIONS:

If an element does not meet the %R criteria, follow the actions stated below:

	PERCENT RECOVERY		
	$\leq$50%	50%-79%	$\geq$120%
Positive Results	R	J	J
Nondetected Results	R	UJ	Acceptable

2. Frequency Requirements

Were Interference QC samples run at the beginning and end of each sample analysis run or minimum of two per 8 hour working shift, whichever is more frequent? YES or NO

If NO, the data may be affected. Use professional judgement to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

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XI. QUANTITATION

List samples/analytes which did not meet QAPP/SAP quantitation limits with an explanation.

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XII. FIELD DUPLICATE PRECISION

Sample Nos.___________,___________ Matrix___________

List the concentrations and RPD of the analytes detected in the field duplicates.

Circle RPDs that do not meet SAP/QAPP criteria.

ANALYTE	SAMPLE CONC.	FIELD DUP CONC.	RPD

9. APPROVAL-

The original copy of this document was approved and signed:

Author	Date
Director, Administration	Date
President, EML	Date

GUIDELINES FOR THE PREPARATION OF STANDARD OPERATING PROCEDURES (SOPS)

FOR

FIELD AND LABORATORY MEASUREMENTS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION V

MONITORING AND QUALITY ASSURANCE BRANCH

QUALITY ASSURANCE SECTION

536 S. CLARK STREET

CHICAGO, ILLINOIS 60605

MARCH 16, 1989

GUIDELINES FOR THE PREPARATION OF STANDARD OPERATING PROCEDURES (SOPS) OF FIELD AND LABORATORY MEASUREMENTS

Field and laboratory protocol for qualitative and quantitative measurements, that are selected for a specific project shall be submitted to the Region V Quality Assurance Section (QAS) as an attachment to the sit-specific Quality Assurance Project Plan (QAPjP) for review/approval prior to the start of the measurement activity.

The field and laboratory measurement protocol should be documented in a standard operating procedure (SOP) format. This SOP shall describe in "cookbook" details the exact instructions to follow and the equipment and materials required to make the measurement.

This document outlines the elements that are to be considered for inclusion in all SOPs.

1. Parameter(s) to be measured.
2. Range of Measurement (Working Linear Range).
3. Limit of Detection. (Where appropriate procedure used for determination of method detection limit shall be specified).
4. Sample Matrix.
5. Principle, Scope and Application.
6. Interferences and Corrective Actions. (Specify method/steps to be taken to eliminate the interferences. Method shall be matrix-specific).
7. Safety Precautions.
8. Sample Size, Collection, Preservation, and Handling (Describing for each matrix which measurement procedure is applicable).
9. Apparatus (including instrument and instrumental parameters) and Materials.
10. Routine Preventative Maintenance, including procedures and frequency.
11. Reagents and Calibration Standards (including preparation procedures, storage and shelf life).

12. Calibration Procedures (including instrument tuning and routine performance checks, etc. If appropriate, specify whether internal standard or external standard techniques are to be used).

13. Sample Preparation (i.e., Extraction, Digestion, etc.)

14. Analytical Measurement (Describing in cookbook detail. Include separate details for each sample matrix if the procedure is applicable to more than one sample matrix).

15. Flow Chart or Table that describes the method step by step.

16. Data Treatment (Details of calculation, including equations).

17. Data Deliverables (define the content of data packages), as a minimum, the following shall be provided:

    a) Case narrative, briefly describe the sample preparation and analysis, problems encountered and corrective action taken during the process of sample preparation and analysis.

    b) Summary of initial calibration and continuing calibration check results.

    c) Summary of Sample Analysis, arranging in increasing order of sample number.

    d) Summary of QC sample analyses.

    e) Raw data including instruments printout, mass spectra, Chromatograms, etc.

    f) Instrument logbook (including serial number, date of purchase, date brought on line, maintenance and repair history over the period of service provided for this specific project. Daily entries should include name of analyst, parameter measured, instrument setting, comments on the sample analysis and any other information that may be deemed of interest.

18. Quality Control Requirements (Specify internal requirements for blanks, spikes, duplicates, and external requirements for reference and QC samples).

19. References.

20. Method Validation Data (if available) should be included to support the validity, limitation and the applicability of the measurement method. If the method is a "Standard Method", i.e., EPA APHA, ASTM or AOAC, this element need not be addressed. If the method has not been validated, then the description of the SOP should include the process for method validation to be conducted for approval prior to the use of the method for sample measurements. If the parameter(s) being measured is for health and safety requirement for field screening to select sampling locations, then method validation data is not required.

STANDARD OPERATING PROCEDURE FOR THE FIELD MEASUREMENT OF VOLATILE ORGANICS BY HNu

I. PARAMETER(S)

Volatile organics with ionization potentials of less than 10.2 eV.

II. RANGE OF MEASUREMENT

The linear range is 0.1-400 ppm, the useful range is 0.1-2000 ppm.

III. LIMIT OF DETECTION

The detection limit of 0.1 ppm was determined by the manufacturer based on the response of benzene at a span setting of 9.8 and a 10.2 eV probe.

IV. SAMPLE MATRICES

Headspace above soil samples collected in split spoon samplers or with trowels.

V. PRINCIPLE, SCOPE AND APPLICATION

The analyzer measures the concentration of trace gases present in the atmosphere by photoionization. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and become a positive ion. This will occur when the ionization potential of the molecule in electron volts (eV) is less than the energy of the photon. The source of photons is an ultraviolet lamp with an energy of 10.2 eV.

Sample gases enter through the inlet into the ion chamber and are exposed to photons emanating from the ultraviolet lamp. Ionization occurs for those molecules having ionization potentials near to or less than that of the lamp. A positive-biased polarizing electrode causes these positive ions to travel to a collector electrode in the chamber. Thus the ions create an electrical current which is amplified and displayed on the meter. This is proportional to the concentration of trace gas present in the ion chamber and to the sensitivity of that gas to photoionization.

In service, the analyzer is first calibrated with a gas of known composition equal, close to, or representative of that to be measured. Gases with ionization potentials near to or less than 10.2 eV will be ionized. These gases will thus be detected and measured by the analyzer. Gases with ionization potentials higher than 10.2 eV will not be detected.

Ionization potentials for various atoms, molecules and compounds are given in the Instruction Manual Appendix. The ionization potential of the major components of air, i.e., oxygen, nitrogen, and carbon dioxide, range from about 12.0 eV to about 15.6 eV and are not ionized by any of the three lamps. Gases with ionization potentials near to or slightly higher than the lamp are partially ionized, with low sensitivity.

VI. INTERFERENCES AND CORRECTIVE ACTIONS

Air currents or drafts in the vicinity of the probe tip may cause fluctuations in readings. Soil, dust, or debris drawn into the probe will result in low readings and/or negative deflection of the meter. High ambient humidity and high percent moisture samples will cause negative deflection of the meter.

To obtain stable, reproducible readings, corrective actions such as shielding the probe from drafts or currents and rain should be done. Sample moisture content is not controllable as representativeness dictates that no special handling of the sample occurs that might bias chemical results. Any drying of the sample would result in loss of volatiles. The field records should indicate which samples were wet and note any negative meter deflection.

VII. SAFETY PRECAUTIONS

Do not look at the light source closer than 6 inches with unprotected eyes. Observe only if necessary, then only briefly. Continued exposure to ultraviolet energy generated by the light source can be harmful to eyesight.

The instrument measures gases in the vicinity of the operator and a high reading when measuring toxic or explosive gases should be cause for action for operator safety.

Use HNu only in an emergency with a low battery when on battery charge.

Turn the function switch on the control panel to the OFF position before any disassembly. Otherwise, high voltage of 1200 vdc will be present. Use great care when operating the analyzer with the readout assembly outside its case due to the presence of 1200 vdc.

Do not interchange lamps of different eV ratings in a probe. Amplifier and components are selected for a specific eV lamp. A probe with the wrong lamp will not operate properly.

VIII. SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING

Soil

Measurement is done on the soil contained in the split spoon sampler or trowel placed in a clean 8-ounce jar with a teflon-lined lid. Measurement should be made within 5 minutes of collection in the field. The jar should be half full.

IX. APPARATUS

- Clean 8-ounce clear glass jars with teflon-lined lid, hole the diameter of the HNu probe drilled in top.

- Duct tape.
- HNu Model PI 101.
- Isobutylene calibration gas cylinder and regulator.
- Spare 10.2 eV lamps.
- Battery charger.

X. ROUTINE PREVENTIVE MAINTENANCE

1. Battery

Check the battery charge during each period of operation, at least once daily. If the battery is low as indicated by the meter reading or the warning indicator, it is necessary to recharge the battery.

2. Lamp

During periods of operation of the analyzer, dust or other foreign matter could be drawn into the probe forming deposits on the surface of the UV lamp or in the ion chamber. This condition is indicated by meter readings that are low, erratic, unstable, non-repeatable, or drifting, or show apparent moisture sensitivity. These deposits interfere with the ionization process and cause erroneous readings. Check for this condition daily. Cleaning can be accomplished as follows:

a. Disassemble the probe and remove the lamp and ion chamber. Exercise great care in doing so to prevent inadvertent damage to these components.

b. First check the lamp window for fouling by looking at the surface at an incident angle. Any deposits, films or discoloration may interfere with the ionization process. Clean the window as follows:

   1) First clean by rubbing gently with lens tissue dipped in a detergent solution.

   2) If this does not remove deposit, apply a small amount of HNu cleaning compound (PA101534) directly onto the lens of the lamp and spread evenly over surface with a non-abrasive tissue (e.g. Kim-Wipe) or a lens tissue.

   3) Wipe off compound with a new tissue.

   4) Rinse with a warm water (about 80°F) or damp tissue to remove all traces of grit or oils and any static charge that may have built up on the lens. Dry with new tissue.

   5) Reinstall lamp in detector and check analyzer operation.

   6) If performance is still not satisfactory, replace the lamp.

3. Ion Chamber

a. Inspect the ion chamber for dust or particulate deposits. If such matter is present, the chamber can be cleaned by removing the outer Teflon ring, and the four screws holding the retaining ring. Carefully move the retaining ring aside (NOTE: this is soldered) and remove the screen. A tissue or cotton swab, dry or wetted with methanol, can be used to clean off any stubborn deposits. The assembly can also be gently swirled in methanol and dried gently at 50-60°C for approximately a half hour. No liquid must be present at reassembly as this would affect the performance. Do not clean the ion chamber with the HNu cleaning compound.

b. Reassemble the probe and check analyzer operation.

c. If performance is still not satisfactory, replace the lamp.

XI. REAGENTS AND CALIBRATION STANDARDS

The calibration gas cylinder containing a certified value of isobutylene is the only reagent/standard. Replace when empty, no shelf life is applicable.

XII. CALIBRATION PROCEDURES

The calibration of the HNu is to be checked daily before field use by using a cylinder of isobutylene (HNu pn 101-350) with a regulator (HNu pn 101-351).

The ppm isobutylene reading, along with the span setting, is recorded in the calibration report contained in the HNu case (35 ppm, span 9.8).

In the field, the calibration must be checked daily before use and readjusted, if necessary, by using this cylinder and regulator as follows:

1. Connect the analyzer to the regulator and cylinder with a short piece of clean tygon tubing.
2. With the SPAN setting at 9.8 and the function switch at the same positions as listed on the Isobutylene Calibration Report, open the valve on the cylinder until a steady reading is obtained.
3. If the reading is 35 ppm, the analyzer calibration is still correct.
4. If the reading has changed, adjust the SPAN setting until the reading is 35 ppm.
5. Shut off the cylinder as soon as the reading is established.
6. Record and maintain this new SPAN setting.

Notes:

A. The regulator sets and controls the flow rate of gas at a value preset at the factory. This will be about 100 to 200 cc/min.; no adjustment to the regulator is necessary in the field.

B. Do not use the cylinder below about 30 psig as readings below that level can deviate up to 10 percent from the rated value.

C. Safely discard the disposable cylinder when empty and do not refill. It is against the law to transport refilled cylinders.

XIII. SAMPLE PREPARATION

A. Soil

Soil obtained in split spoon samplers or by a hand trowel/corer should be placed in a clean 8-ounce clear glass jar outfitted with a teflon-lined lid with a hole the diameter of the HNu probe drilled in it. Fill the jar half full, close tightly (lid hold should be covered with duct tape) and allow to equilibrate for 2 minutes before measurement.

XIV. ANALYTICAL MEASUREMENT

1. Unclamp the cover from the main readout assembly.

2. Remove the inner lid from the cover by pulling out the two fasteners.

3. Remove the probe, handle and cable from the cover. Attach the handle to the front part of the probe.

4. Connect the probe cable plug to the 12 pin keyed socket on the readout assembly panel. Carefully match the alignment slot in the plug to the key in the connector. Screw down the probe connector until a distinct snap and lock is felt.

5. Screw the probe extension into the probe end cap. The probe may be used without the extension if desired.

6. Set the SPAN control for 10.2 eV as specified by the daily in-field calibration with isobutylene.

7. Turn the function switch to the BATT (battery check) position. The needle on the meter will go to the green zone if the battery is fully charged. If the needle is below the green arc or if the Low Battery Indicator comes on, the battery must be recharged before the analyzer is used.

8. Set SPAN pot to 9.8.

9. Turn the function switch to the STANDBY position. Turn the zero adjustment until the meter needle is at zero.

10. Calibrate the instrument daily as described in Section 12.

11. Turn the function switch to the appropriate operating position. Start with the 0-2000 position and then switch to the more sensitive ranges. The UV light source should be on, confirmed by briefly looking into the probe to observe the purple glow from the lamp.

12. Peel back the duct tape from the lid and place the HNu probe in the hole. Record the reading on the Soils Data Form.

13. After completion of each days measurements, check battery condition as described in No. 7.

14. Turn function switch to OFF position.

15. When not operating, leave analyzer in assembled condition, and connected to battery charger.

16. When transporting, disassemble probe and extension from readout assembly and return equipment to its stored condition.

17. In case of emergency, turn function switch to OFF position.

XV. FLOW CHART

Not applicable.

XVI. DATA TREATMENT

Not applicable, instrument provides direct real time readout in ppm units.

XVII. DATA DELIVERABLES

Record calibration details on Field Instrument Calibration Log and results on Soils Data Form.

XVIII. QUALITY CONTROL REQUIREMENTS

Each day an upwind location will be used to determine the ambient background level. One location for every ten will be selected for measurement as a field duplicate. Two separate aliquots of soil will be placed in two 8-ounce jars. No rpd limits have been established for field duplicate precision. Record both reading on the Soils Data Form.

XIX. REFERENCES

- Instruction Manual, HNu Model PI 101 Portable Ionization Analyzer, December, 1985.
- HNu Systems (617) 964-6690

XX. METHOD VALIDATION DATA

Not applicable as volatile organics are being measured for field screening purposes to select sampling locations for chemical analysis.

Standard Operating Procedure
for the
Measurement of pH in the Field
Using the Fisher Accumet Model 955 Portable
pH/mV Temperature Meter

1. Parameter to be measured: pH.

2. Range of Measurement: 0.00 to 14.00 pH units.

3. Sample Matrix.

This method is applicable to drinking, surface, saline, and groundwater samples; chemical domestic and industrial wastes; leachates.

4. Principle, Scope, and Application.

The pH of a sample is determined electrometrically, using a combination sample-reference pH electrode.

5. Interferences and Corrective Action.

5.1 Any sample constituent which coats the electrode can cause sluggish response. This can be eliminated by cleaning the electrode according to manufacturer's instructions.

5.2 Temperature effects on the electrometric measurement of pH arise from two sources. The first source is caused by change in electrode output at various temperatures. This is avoided by using the Automatic Temperature Compensation (ATC) probe. The second source is the change of pH inherent in the sample at various temperatures. Therefore, the sample temperature should be reported with the pH.

6. Safety Precautions.

Common sense will eliminate the possibility of any hazards while the portable pH meter is being used. Obviously, buffers and field samples must never be pipetted by mouth. Handle the electrode carefully to avoid breakage. Since the electrode will be measuring potentially hazardous material and all pH electrodes leak small quantities of electrolytes, they must never be placed in the mouth.

7. Sample Size, Collection, Preservation, and Handling.

Collect approximately 50 ml or more of the sample to be measured. To avoid the possibility of cross contamination from sample to sample and contamination of leaking electrolyte, the samples will be discarded after pH measurement and not used for any other parameters. If for any reason the pH cannot be taken immediately in the field, samples must be stored at 4°C and measured within a 24-hour period.

8. Apparatus and Materials.

8.1 Fisher Accumet Model 955 Portable pH/mV Temperature Meter
8.2 Three or more 50 ml plastic beakers
8.3 Commercially prepared pH 4.01, 7.00, 10.00 buffers
8.4 Squeeze type wash bottle, 125 ml or larger
8.5 Distilled water
8.6 Electrode; extra electrolyte for filling if necessary
8.7 Automatic Temperature Compensation (ATC) Probe
8.8 One or two 9-volt transistor batteries

9. Routine Preventive Maintenance.

9.1 The instrument and batteries should be checked and calibrated in the laboratory before the field effort begins.
9.2 The accuracy of the buffer solutions used for field and laboratory calibration should be checked. Buffer solutions need to be changed due to degradation upon exposure to the atmosphere. (The date of preparation of each buffer should be included on the bottle label.) Record source of buffer and date opened on Field Meter Log Sheet.
9.3 Immerse the tip of the electrodes in water overnight. If this is not possible due to field conditions, immerse the electrode tip in water for at least an hour before use. The electrode tip may be immersed in a rubber or plastic sack containing buffer solution for field transport or storage. This is not applicable for all electrodes, as some must be stored dry.
9.4 Make sure all electrolyte solutions within the electrode(s) are at their proper levels and that no air bubbles are present within the electrode(s).
9.5 Distilled water pH and conductivity should be monitored periodically.
9.6 The electrode should be stored and cleaned according to manufacturer's instructions.

10. Reagents and Calibration Standards.

Commercially prepared standardized buffers of pH 4.01, 7.00, and 10.00 are used to calibrate the instrument. The source and date opened will be recorded on the Field Meter Log Sheet.

11. Calibration Procedure.

<u>Fisher Accumet Model 955 Calibration</u>

To measure the pH values of samples that vary over a range wider than two pH units, a two-point calibration will be done daily before field use to compensate for less than 100 percent electrode efficiency. The STANDARDIZE control provides the first set-point. The slope control sets the second set-point.

At pH 7, this "slope" adjustment has no effect on the readings. As readings increasingly differ from pH 7, the adjustment's effect becomes more pronounced - always in the opposite direction from one side of pH 7 to the other. Therefore, both calibration set points should be on the same side of pH 7.

Choose two buffer solutions with values that bracket the desired measuring range, usually pH 7 and pH 10 for groundwater and surface water. The buffer closest to pH 7 in value should always be used for the first set-point (with the STANDARDIZE control), and the buffer furthest from pH 7 in value should always be used for the second set-point (with the SLOPE control).

pH 7 Buffer Calibration:

a. Observe that electrode lead is securely connected to INPUT jack on instrument top panel. Also be sure to remove protective cot from tip of supplied combination electrode.
b. Observe that plug of ATC Probe is securely connected to °C jack on instrument right-side panel.
c. Obtain pH 7 buffer and ensure that buffer temperature is within 10°C of sample temperature.
d. Immerse electrode system and ATC Probe into buffer solution.
e. Set FUNCTION selector to °C position and place ON-OFF switch to ON position. Set the slope control full counter clockwise.
f. Allow electrode system and buffer solution to reach thermal equilibrium (°C reading steady), then determine exact pH of buffer solution from the table of buffer pH versus temperature found on the bottle label.
g. Set FUNCTION selector pH position, then adjust STANDARDIZE control until digital display indicates the pH value of buffer solution.
h. Remove electrode system and ATC Probe from buffer solution and rinse them with distilled water.

pH 10 (or 4) Buffer Calibration:

a. Immerse the electrode system and ATC probe into the pH 10 buffer.
b. Set the FUNCTION selector to C position. Allow the electrode system and buffer solution to reach thermal equilibrium (°C reading steady), then determine the exact pH of the buffer solution from the table of buffer pH versus temperature found on the bottle label.
c. Set the FUNCTION selector to the pH position, then adjust the SLOPE control until the digital display indicates the pH value of the buffer solution.
d. Remove the electrode system and ATC probe from the buffer solution and rinse with distilled water.
e. The pH meter is now ready for sample measurements.

Notes:

Thermal equilibrium normally requires about 1 minute, but will vary depending upon temperature difference between electrode system and buffers.

12. Sample Preparation.

There is no sample preparation for this procedure other than allowing the electrode system and sample solution to reach thermal equilibrium (steady thermometer reading).

13. Analytical Measurement.

13.1 Calibrate the instrument (See Section 11).
13.2 Remove electrode system and ATC Probe from buffer solution and rinse them with distilled water.
13.3 Immerse the electrode system and ATC Probe into the sample solution and allow sufficient time for the electrode system and sample solution to reach thermal equilibrium.

Notes: Thermal equilibrium normally requires about 1 minute, but will vary depending upon temperature difference between electrode system and sample.

13.4 Read the pH value of sample from the digital display and record on the Well Purging and Sample Collection form. Remove electrode system and ATC probe from sample and rinse with distilled water. Repeat step 13.3 and 13.4 for remaining samples.
13.5 ON-OFF switch to OFF after last measurement.

14. Data Deliverables.

The pH accuracy will be assessed by performing two measurements on three standard buffer solutions. Each measurement will be within $\pm$0.05% standard unit of the certified value for the buffer solutions. Precision will be assessed through replicate measurements on field samples. The standard deviation of four replicate measurements must be less than or equal to 0.1 standard unit. The electrode will be withdrawn, rinsed with dionized water, and re-immersed between each replicate. Calibration and verification will be done in the field before the first replicate and after the last. The instrument used will be capable of providing measurements of 0.01 standard unit. The instrument will be calibrated at least once daily and every 10 samples and results recorded on the Field Meter Instrument Calibration Log. Field replicates will be done at a frequency of every 10 samples. This will be done in quadruplicate. All field sample measurements will be recorded on the Well Purging and Sample Collection form.

15. Quality Control Requirements.

Quadruplicate samples will be done every 10 samples by rinsing the electrode after the initial reading, waiting 1 full minute, and then measuring the next sample. The standard deviation of four replicate measurements must be less than or equal to 0.1 standard unit.

16. References.

Material for this SOP was obtained from the Instruction Manual for the Fisher Accumet Model 955 Portable pH/mV Temperature Meter, Catalog No. 69348.

17. Method Validation Data.

The parameter of pH is being measured for field screening to select sampling locations and method validation data is, therefore, not required.

Standard Operating Procedure
for the
Measurement of Specific Conductance in the Field
Using the Cole Parmer Model 4070 Conductivity Meter

1. Parameter to be measured: Specific Conductance.

2. Range of Measurement:

Range
(a) 0 to 19.99 mS
(b) 0 to 1999 uS
(c) 0 to 199.9 uS
(d) -30.0 to $\pm$150.0°C

Resolution
(a) 0.01 mS
(b) 1 uS
(c) 0.1 uS
(d) 0.1°C

3. Sample Matrix.

This method is applicable to drinking, surface, saline, and groundwater samples; domestic and industrial wastes.

4. Principle, Scope, and Application.

The specific conductance of a sample is measured using a self-contained portable conductivity meter equipped with an Automatic Temperature Compensation (ATC) probe.

5. Interferences and Corrective Action.

5.1 Precipitation reactions and absorption of carbon dioxide from the air can affect the specific conductance. This can be avoided by taking the measurement as soon after sampling as possible.
5.2 Specific conductance is affected by temperature changes. The use of the ATC probe will eliminate this problem.
5.3 Any constituent of the sample which can coat the conductivity probe such as oil or grease, algae, or sedimentation can cause incorrect or sluggish response. Dried salts or particulate matter allowed to build up on the cell plates may cause the readings to be erroneous. It is important to rinse the cell carefully with deionized water.
5.4 Ensure that no air bubbles are trapped in the cell area between the plates. Failing to do so could cause a false reading.

6. Safety Precautions.

Common sense is the best safeguard against any potential hazards. Obviously, one must never pipette samples or standard solutions by mouth. Handle the probes carefully to avoid breakage. Since the meter will be measuring potentially hazardous material, the probes must never be placed in the mouth.

7. Sample Size, Collection, Preservation, and Handling.

Samples should be collected in clean glass or plastic containers. The volume should be such that the cell plates of the probe are completely immersed in the sample. Samples may be filtered through a 4.5 m filter before analysis if necessary. Specific conductance should be measured as soon after sampling as possible, however, if readings cannot be taken immediately, samples should be stored at 4°C and measured as soon as possible.

8. Apparatus and Material.

8.1 Cole Parmer Conductivity Meter, Model 4070
8.2 Conductivity probe
8.3 Automatic Temperature Compensation (ATC) probe
8.4 Clean sample containers
8.5 Squeeze-type wash bottle, 125 ml or larger
8.6 Deionized water
8.7 Calibration standard solution
8.8 Laboratory wipes - KimWipe or equivalent
8.9 Replacement batteries, types PP3, 6F12, or MN1640

9. Routine Preventative Maintenance.

It is necessary to keep the external surfaces clean and free from dust.

All conductivity probes should be thoroughly rinsed after use and stored in deionized water. Particular care should be taken to ensure that the electrical connections are free from dirt and debris. It is recommended that the instrument be checked and calibrated before going into the field. The symbol "BAT" will appear on the display if the batteries need replacing.

10. Reagents and Calibration Standards.

Potassium chloride standard solutions with a specific conductance closest to the values expected in the field should be used. The table below may be used for guidance:

SPECIFIC CONDUCTANCE OF KCl SOLUTIONS AT 25 DEGREES CENTIGRADE

Concentration	Specific Conductance	
mol/l	mg/l	umhos/cm
0.0001	7.456	14.94
0.0005	37.28	73.90
0.001	74.56	147.0
0.005	372.8	717.8
0.00702	523.4	1000
0.01	745.6	1413
0.02	1591.2	2767

NOTE: This table has been modified from Standard Methods for the Examination of Water and Wastewater (1980).

Standard solutions may be stored at 4°C for up to one week. Date of preparation can be noted on the container and on the Field Meter Instrument Calibration Log.

11. Calibration Procedures.

Cole Parmer Model 4070 Conductivity Meter

Two options for calibration of the Model 4070 are available in the field, depending on instrument accessory availability. If the pre-calibrated probe is available, this is the easiest calibration procedure to do in the field. However, if the probe is not available, calibration will have to be done daily before field use with a standard solution (commercially prepared):

Calibration with Pre-Calibrated Probe:

a. Connect a standard pre-calibrated probe to the unit.
b. Select the "Set K" position on the function switch.
c. Adjust the "Set K" control until the display indicates the value of the cell constant as marked on the probe being used.
d. The standard X 1.0 probe has a cell constant range from 0.80 to 1.20 and is calibrated to 2 decimal places. The display should be set to indicate this figure exactly.

   The standard X 10 probe has a cell constant range from 8.0 to 12.0 and is calibrated to 1 decimal place. The display should be set to indicate this figure shifted one place to the right.

   The standard X 0.1 probe has a cell constant range from 0.08 to 0.12 and is calibrated to 2 decimal places. The display should be set to indicate this figure shifted one place to the left.

d. Before using the 20 uS range, the probe should be thoroughly rinsed in deionized water, excess water shaken off and the outside of the probe body wiped dry. The display should then be set to zero, with the probe in free air, by using the "Zero 20 uS" control.

Calibration with a Standard Solution:

a. Select the "COND" range.
b. Immerse the conductivity cell and A.T.C. probe (if separate probe is being used) into the prepared standard.
c. Select the 2000 uS range if using a 1000 uS or 1413 uS standard or other suitable range if an alternative standard is being used.
d. Adjust the "Set K" control to give the exact readout of the standard solution selected on the display.
e. After carrying out the calibration with standard solutions as detailed above and with the probe still in the standard solution and the display set to the value of the standard solution, switch to the "Set K" range to give a direct readout of the cell constant.

f. If the readout cannot be set to the value of the standard solution with the "Set K" control, then the cell constant lies outside the "Set K' range of 0.80 to 1.20. In such cases, the display should be set to read 1.00 on the "Set K" position, the display reading on the range giving the best resolution should be noted and the cell constant calculated from the following formula:

$$K = \frac{\text{Conductivity of Standard Solution}}{\text{Display Reading}}$$

This figure should be noted and (with the cell constant set to 1.00 on the "Set K" position) the display reading should be multiplied by this figure to obtain the correct conductivity.

Note:

Ensure that the conductivity standard has not reached or gone over the expiration date marked on the container.

12. Sample Preparation.

If the sample contains a great deal of particulate matter which may interfere with readings, they may be filtered through a 4.5 m filter.

13. Analytical Measurement.

13.1 Calibrate the instrument (See Section 11).

13.2 Rinse the conductivity probe and the ATC probe thoroughly with deionized water, shake to remove internal droplets, and the outside should be wiped before immersing into sample.

13.3 Allow the readout on the instrument to settle (usually about one minute). Multiply the instrument readout by the correction factor determined during calibration. Record the corrected conductivity on the Well Purging and Sample Collection form.

13.4 Step 13.2 should be repeated after every sample to prevent cross-contamination.

13.5 On completion of sample measurement, the probes should be thoroughly rinsed in deionized water and for short term storage should be kept immersed in deionized water so that the plates remain wetted. For longer term storage, the probes should be thoroughly rinsed in deionized water, the outside of the probes wiped dry, and the probes stored dry. It should be noted that it may take some time for stability to be achieved when a dry probe is first used while the plate becomes re-wetted.

14. Data Deliverables.

Initial calibration of the instrument and continuing calibration check results will be recorded on the Field Meter Instrument Calibration Log form. Summary of sample analysis will be recorded on the Well Purging and Sample Collection form, including sample duplicates.

15. Quality Control Requirements.

The meter will be read to the nearest 10 umhos/cm within a range of 0 to 20,000 umhos/cm. Accuracy of measurements shall be ±5 percent of a standard. The meter will be calibrated at least once daily and after every 10 field samples. Field duplicates will be measured at a frequency of every 10 samples by thoroughly rinsing the probes in deionized water, waiting one full minute, and then immersing probes in the duplicate sample. Precision shall be a standard deviation of ±10 percent.

16. References.

Material for this SOP was obtained from the Instruction Manual for the Cole Parmer Model 4070 Conductivity Meter.

17. Method Validation Data.

The parameter of specific conductance is being measured for field screening to select sampling locations, and method validation data is, therefore, not required.

APPENDIX B

LABORATORY QUALITY ASSURANCE PLAN

Prepared by Core Laboratories, Inc. New Jersey Location (Core)
284 Raritan Center Parkway, P.O. Box 7808
Edison, New Jersey 08818-7808
(908) 225-6700

Core Approval

Stephen R. Grant 2/2/96
Laboratory Manager Date

[illegible] M. [illegible] 1/31/96
Quality Assurance Officer Date

852
Document No.

FOREWORD

The Core Laboratories, Inc. environmental testing laboratory in Edison, New Jersey has provided high quality analytical and data management services to major industrial corporations, waste disposal firms and governmental agencies since 1981. The laboratory's specialized services are directed at the accurate measurement of contaminants in water, soils and sediments, and hazardous wastes. Laboratory services have been developed in direct response to regulations written and enforced by federal and state environmental agencies. The laboratory has historically performed special project investigations that have enhanced its competence and versatility in the field of analytical chemistry. This facility previously operated as ETC and PACE, and recently became part of Core Laboratories, Inc., effective December 23, 1995.

Core Laboratories, Inc., an international company with headquarters in Houston, Texas, provides environmental and petroleum testing services at laboratory locations within the United States of America and in Canada, Indonesia, Malaysia, Scotland and Venezuela. Figure 1.1 shows current laboratory locations. Within this network is extensive analytical capacity, capability and expertise. This written quality assurance plan documents the procedures used to manage custody elements and analytical processes at the Core Laboratories, Inc. New Jersey location (Core) and is consistent with the level of quality and integrity represented by the corporate organization. *Core* is utilized throughout this document to reference the specific New Jersey location.

This quality assurance plan has been prepared to conform in content with the USEPA QAMS-005/80, "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans", December 29, 1980. QAMS-005/80 includes a section titled *Project Description*. In this document, the laboratory policy statement replaces specific project description information. The tables and figures referenced throughout the document are found in the appendix. The appendices of project specific quality assurance documents may include additional elements or information.

This document describes ongoing laboratory operations for routine analyses performed at Core. As such, the material contained within is subject to change. Changes may be based on specific project requirements or procedural system modifications geared towards operational process and quality improvements. This document is reviewed and updated on a minimum yearly basis.

Because of the variability of samples and matrices, it is not unusual to find that the performance criteria of a particular method is unachievable on particular samples. In such circumstances, any method or criteria modification will be noted in each final report.

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Figures & Tables

STATEMENT OF POLICY

The Core Laboratories, Inc. quality objective is to provide clients with technically and legally defensible data of known and documented quality. Quality is defined as conformance to requirements. The Core Laboratories, Inc. *Quality Policy* is as follows:

Quality Policy

We will provide on-time, error-free service, data, reports, and products which meet or exceed our customer's requirements and/or applicable industry standards.

We will practice error prevention rather than error correction.

We will perform each task right the first time.

Each laboratory staff member must adhere to and practice the Core Laboratories, Inc. *Analyst's Commitment to Quality*, which follows:

Analyst's Commitment To Quality

To produce results that are accurate and defensible.

To use approved methodology and procedures. Deviations from methodology or procedures must be approved and documented.

To acquire a full understanding and knowledge of the methodology used and he associated requirements.

To apply the necessary quality control measures to ensure the accuracy, precision, and completeness of all analyses and resulting data.

To document all test findings and details in such a way that results can be regenerated at a later date by another person.

To utilize good laboratory practices throughout all phases of the analysis process.

To act on identified non-conformances and out of control events in a timely manner and to apply the necessary corrective action.

To provide the client with data of known and documented quality and to advise the client of data that does not meet the method specifications or the client requirements.

To provide accurate and complete information to management and auditors that is verifiable and traceable to associated documentation.

ORGANIZATION AND RESPONSIBILITY

Organizational charts for Core Laboratories, Inc. are shown in Figures 4.1. and 4.2. Figure 4.1 illustrates corporate relationships, including the analytical laboratory component. Figure 4.2 demonstrates the organization of the Core Laboratories, Inc. Edison, New Jersey location (Core).

As shown in Figure 4.2, Core's organizational structure allows close, coordinated interactions and promotes the common goals of successful project management and quality data. Core's quality assurance staff is independent of laboratory operations and reports directly to the Laboratory Manager. Each individual in the Core organization is responsible for their product or the service they perform. Analysts and technicians who handle samples or analytical data have the following minimum responsibilities.

- o Performs the expected services and methodologies.
- o Performs the quality requirements of their tasks.
- o Takes the corrective actions described in the analytical methods or protocols when the quality control specifications are not met.
- o Accurately communicates any sample or quality problems to responsible management personnel.
- o Ensures that sample custody is maintained.
- o Adheres to the Core Laboratories, Inc. *Analyst's Commitment to Quality*.

Project Organization

Projects at Core are monitored by project teams selected prior to project initiation. The teams consist of representatives from the laboratory operations, quality assurance and marketing staff. The goal is to set up and monitor the project to meet client needs. Figure 4.3 presents the key individuals on the Core project team. The minimum responsibilities for key project personnel are as follows.

Account Executive

- o Supports client regulatory programs.
- o Coordinates preproject meetings.
- o Establishes contractual terms and conditions.
- o Provides oversite of the project.
- o Communicates the client's quality needs.

Project Manager

- Serves as primary client contact for the project.
- Provides advisory consultation to clients on regulatory and technical issues.
- Attends preproject and project progress meetings; assists in client or project audits.
- Defines project scope through detailed documentation of client and project quality and technical requirements.
- Communicates the client and project quality and technical requirements to laboratory personnel; implements the project.
- Coordinates field activities with sample management personnel to ensure proper delivery of shipping containers, sample bottles, etc.
- Tracks and manages the project through the laboratory.
- Updates the client on nonconformances and responds to requests for information.
- Coordinates technical report generation to ensure client commitments are achieved.

Laboratory Manager

- Provides supervision of laboratory operations.
- Implements the laboratory quality assurance plan.
- Ensures proper scheduling and execution of testing programs.
- Assures that quality assurance and quality control criteria of analytical methods and projects are satisfied.
- Assesses data quality and takes corrective action when necessary.
- Notifies the project team of specific laboratory nonconformances and changes.
- Approves and releases technical and data management reports.
- Ensures that analysts and technicians maintain sample custody in the laboratory.
- Approves project specific laboratory quality assurance plans.
- Coordinates management of projects through technical supervisors.

Quality Assurance Officer

- o Acts as the official organizational contact for quality assurance matters. Concerns may include, but are not limited to, quality assurance plans, standard operating procedures, analytical methodologies and protocols, audits, certifications, support services and corrective actions.
- o Identifies and responds to quality assurance needs, assists in problem resolution and answers requests for guidance, information or assistance.
- o Provides guidance in the development of quality assurance plans.
- o Reviews, evaluates and approves written quality assurance plans.
- o Tracks the progress of quality assurance tasks (from preplanning to data assessment) and consults periodically with project managers.
- o Monitors quality assurance, quality control and corrective actions throughout the laboratory facility.
- o Provides the Laboratory Manager reports of laboratory performance.

QUALITY ASSURANCE OBJECTIVES

The Core Laboratories, Inc. quality assurance program objectives are as follows:

- o Define the requirements for laboratory performance,
- o Train laboratory staff on the requirements, and
- o Assess laboratory compliance on the requirements.

These practices ensure that the laboratory produces data which meets the quality requirements of the methods in use and the quality objectives of the data user. By accomplishing this objective, the data user will be able to employ the laboratory data for its intended use.

In addition, these practices provide management with data quality and operational performance feedback. Performance feedback data enables management to determine if the laboratory facility is achieving the established quality and operational standards of the environmental laboratory industry. It enables Core to assess operational performance from a quality perspective and perform corrective action as necessary.

The quality assurance objectives of the laboratory must be consistent with specifications for analytical services cited for projects and samples. The laboratory will perform analytical services and support in accordance with project requirements as specified by the client.

The data quality objectives of the laboratory are to produce complete, valid, and verifiable data. Core's goals are to execute the required methodologies and procedures, and to generate precise and accurate measurements. Tables 5.1, 5.2 and 5.3 identify the laboratory's routine quality control objectives.

SAMPLING SERVICES

Field Support

Core provides shipping containers, custody documents, custody seals, sample bottles, labels, chemical preservatives for water samples, "blue ice" packs to maintain thermal preservation, and trip and field blanks to support field sampling events. Table 6.1 lists sample container types, preservatives and holding times. Core can provide pick up and delivery services to its clients.

Upon receipt of the field samples at the laboratory, Core ensures that sample bottles are maintained according to preservation requirements and that sample storage conditions do not contribute to the presence of test analytes in the samples.

Core Shipping Containers

The Sample Shuttle™ was developed in 1981 by laboratory staff for the transport of environmental samples from the field to the laboratory. The Sample Shuttle is a rugged carrying case lined with insulating polyurethane. Insulating sleeves with pre-formed slots hold the sample bottles. The container is lockable from the outside. Chain-of-custody seals and forms, employed for each Shuttle packed at Core, ensure complete documentation and provide evidence of unbroken custody of the Shuttle contents. The Shuttle meets or exceeds all protocol requirements (i.e., DOT, USEPA, ASTM) for shipping. Figure 6.1 lists instructions for Sample Shuttle use and sampling notes. The Shuttle is configured at the laboratory to provide the client with all of the sample containers needed for the analyses.

Core Shuttles and/or commercial coolers are utilized for projects based upon the preference of the client. The commercial coolers are, likewise, sealed and provide the above listed items for sampling events and custody documentation. In this document, generic references to Sample Shuttles will apply to commercial coolers as well.

Preservation

Core provides the required chemical preservatives for water samples and "blue ice" packs, for thermal preservation at 4 +/- 2° C, in the shipping containers during the shipping process. High quality reagent grade chemical preservatives are used. The ice packs are supplied at pre-frozen or ambient temperatures based upon the client's needs. It is the responsibility of those collecting the samples to properly use these materials and ensure that proper preservation techniques are performed and preservative requirements are met. Core recommends that all sample containers be chilled with ice after collection prior to shipment in the Sample Shuttles.

Upon receipt of samples at the laboratory, the temperature of each Shuttle is measured and recorded on the chain of custody documents. Similarly, the pH of bottles to which chemical preservative was added is measured (with the exception of sample collected for volatile organic compounds), and the check recorded. A disposable pipette is used to remove an aliquot of the sample for the pH check. When deviations from the required chemical or thermal preservation are noted, the project manager is notified, and clients may become involved with determining a course of action to follow.

Water samples for GC and GC/MS volatile aromatics determinations are monitored for pH within 24 hours of sample log-in. The pH is initially checked by testing the contents of the sample bottles used during volatiles screening procedures. The remaining bottles are not opened until analysis, at which time the pH of each individual sample bottle used is checked. Samples that have an observed pH > 2 upon initial monitoring are scheduled for analysis with a shortened hold time of 7 days from sampling. The portion of sample used for the analytical determination is removed from the vial prior to checking the sample's pH. Sample pH measurements are recorded on laboratory chronicles as they are taken.

Sample Bottles

Core provides precleaned sample bottles in the shipping containers for sample collection. Used sample bottles are never reused by the laboratory. Vendor prepared I-Chem 200™, 300™ or equivalent bottles can be provided as projects necessitate. Laboratory cleaning and preparation procedures for commonly used bottles are as follows.

Bottle Caps: Teflon lined. New caps are rinsed with deionized water, allowed to air dry in racks, then placed on bottles.

Amber Glass Bottles (1 L, 500 ml, 250 ml): Rinsed with de-ionized water. Baked at 200° C for 30 minutes prior to capping and use.

Clear Glass Vials (40 ml for volatile organics): Teflon lined septa for caps are stored in containers prior to use. Bottles, caps and septas are rinsed with de-ionized water, then baked for one hour at 105° C in an oven used exclusively for this purpose. Hydrochloric acid preservative is added to each vial used for aqueous samples. Upon client request 20 mg of sodium thiosulfate is added to remove residual chlorine in the sample. Bottles are capped and stored in sealed, air-tight metal containers prior to use. Bags of granulated carbon are enclosed to adsorb any organic vapors present.

Amber Glass Bottles (125 ml): Rinsed with de-ionized water and air dried. Baked at 200° C for 30 minutes prior to capping and use.

Plastic Bottles: Bottles and caps are rinsed with deionized water and allowed to air dry in racks prior to capping and use. Bottles used to collect sample for the analysis of metals are rinsed in nitric acid solution.

Coliform Bottles: All bottles used for the sampling and analysis of coliform are purchased sterilized. They are received sealed and autoclaved.

Sample Receipt Schedule

Samples are normally delivered to the Core facility during normal business hours within one day following field sampling unless different arrangements are made in advance with an authorized Core representative. Shipping containers received at the laboratory on business holidays, weekends or after normal work hours will be placed in the walk-in refrigerator and opened on the next regular business day unless prior arrangements are made in advance for that day's receipt and log-in.

SAMPLE CUSTODY

Areas of Concern

The chain of custody in the laboratory consists of two areas of concern:

- o Receipt and log-in of samples; and
- o Internal custody of samples transferred throughout the laboratory.

Samples are physical evidence and, as such, are handled at Core according to certain procedural safeguards. For some types of legal proceedings, a showing to the court that the custodial laboratory is a secure area may be all that is required for sample data to be admitted as evidence. In other cases, the court may require a detailed showing of the hand-to-hand changes of custody that a sample has undergone. Federal and state agencies and private sector clients may also require varying levels of custody documentation from the laboratory. Core is equipped to provide the defined level of custody documentation necessary.

Maintaining Custody by NEIC Definition

Custody is maintained by USEPA National Enforcement Investigations Center (NEIC) definition when:

- o The sample is in the actual possession of the responsible person, or
- o The sample is in the responsible person's view after being in their possession, or
- o The sample is in the responsible person's possession and then they locked or sealed it up to prevent tampering, or
- o The sample is in a secure area.

Core Laboratory Procedures

To satisfy these custody provisions, the following standard operating procedures are employed:

- o The Core laboratory is maintained as a limited access, secured facility.
- o The grounds and parking areas around the building are patrolled on a regular basis by a roving patrol supplied by the Raritan Industrial Center.
- o Employee access to the building and selected security area (including walk-in refrigerators) within the building is controlled by a computerized card reader employee identification system. Access is on a need basis during authorized work hours.
- o Visitors must register upon entering the lobby of the facility, and must be accompanied by their host at all times while they are in the building.

- o Receipt and log-in of samples is fully documented and is performed in a controlled area.
- o Samples are stored in a secure area.
- o Walk-in refrigerators, freezers, and other primary sample storage areas are kept locked at all times or when unattended, dependent upon the function of the unit.
- o Only designated Core personnel have access to the primary sample storage areas.
- o Samples remain in secured sample storage until removed for sample preparation or analysis.
- o The internal transfer of samples is controlled and documented.

Core Sample Custodians

Core sample custodians are responsible to perform the following:

- o Receive, inspect and record the condition of samples and shipping containers.
- o Sign appropriate documents shipped with the samples.
- o Verify and record correctness of sample documentation.
- o Place samples into appropriate storage and secure areas.
- o Control and monitor access and storage of samples.

Sample Identification Numbers

Unique Core sample identification (ID) numbers are assigned to client samples. Every sample bottle is labeled with the client and laboratory ID. Coded descriptions of the required analytical and support services are associated with each sample number. The Core sample ID code is used to track the sample pathway throughout the analytical process.

If samples are "prelogged" in the laboratory information management system (LIMS) prior to shipping (Core numbers are already assigned), the bottle labels include the ID codes, and the Core sample numbers are utilized during the laboratory shipping, receipt and log-in procedures. If laboratory ID numbers are to be assigned after bottle shipment or upon sample receipt, plain or fill-in labels are shipped. The client sample IDs are then used during laboratory receipt and log-in processes.

Sample Receipt and Log-In

The sample custodian is responsible for laboratory receipt and log-in operations. The sample custodian examines the shipping containers, custody seals and shipping documents. The shipping containers are opened, the temperatures taken, and all samples checked against the accompanying paperwork. The pH of sample aliquots which have been chemically preserved, except those used for volatile organics analyses, are monitored. Any and all noncompliances are documented. The client is contacted by telephone as soon as practical regarding any custody problems or problems with the condition of the samples upon receipt at the laboratory.

Should the samples arrive before all the necessary information is received from the client regarding analysis, the clock will not start (days will not be counted towards turnaround) until the information is obtained; actual sample holding time is independent and not affected by any delay. Turnaround is defined as the time interval between laboratory receipt of a sample in a condition suitable for the prescribed analysis and delivery of analytical results to the client.

Sample turnaround may be based upon single sample receipt at the laboratory or the receipt date of the last sample of a sample delivery group (SDG) received at the Core facility. SDG is defined by the following, whichever is more frequent: each twenty (20) field samples received or each fourteen (14) day calendar period during which field samples are received following the first in the group. Samples may be assigned to SDGs by matrix (aqueous and soils/sediments placed in separate SDGs) at the discretion of the laboratory. The turnaround time is based upon the analytical protocol or as defined by the client.

During log-in, the sample custodian checks the contents of the shipping containers against the Core custody documents, Chain of Custody Form 1 (CC1) for single samples or Chain of Custody Chronicle for multiple samples, Figure 7.1 - 7.3, or other client supplied custody records. In the absence of comparable shipping records, a Core Line Chain of Custody Form, Figure 7.4, is generated. Observations concerning the presence or absence of bottles, the condition of the samples as received and any other anomalies are recorded on the custody forms and Sample Receipt Checklist, Figure 7.5.

The original custody form is signed by the sample custodian, documenting sample receipt by the laboratory. Completed custody forms are placed into file folders identified by unique log-in codes specific for the samples. The file folders are reviewed by the project managers and ultimately transferred to report production personnel who incorporate the custody forms into the report packages, and assume responsibility for proper Core custody records archive along with the sample data.

When receipt documentation is completed, a Core sample Log-in Form, Figure 7.6, is generated. A log-in form reflects the information present in the LIMS for the sample. A log-in form is an internal document designed to summarize all the relevant information concerning a sample's receipt and analytical requirements. It is circulated internally and instructs the laboratory with regards to the receipt, and required analyses and reporting of the sample. Each sample bottle is labeled with its unique log-in code reference, as well as its sample identification number.

After the samples are logged-in, the sample bottles are placed in designated areas of the cold storage units. The sample bottles are stored according to preservative type and analyses in log-link order. Volatile organic sample bottles are stored in a separate refrigerator unit.

Sample Custody for Client Drop Off or Core Courier Pick Up

The transfer of shipping container custody is documented on a Daily Receipt Log, Figure 7.7. If the client wants a copy, it is provided for their records. The Core courier is not authorized to open shipping containers or itemize samples for laboratory receipt.

If the client drops off samples at the Core facility and requests a showing of hand-to-hand change of sample custody, the shipping containers are opened by the sample custodian and the samples are itemized. The checks and notations previously described are made. The client is given the custody forms to review. The client signs the Chain of Custody form, relinquishing the samples to the sample custodian. A copy of the Chain of Custody form serves as a receipt for the client if one is requested. Standard log-in procedures are follow.

Special Handling for High Hazard Samples

If a shipping container is labeled "Caution - Hazardous Materials," or if it contains samples suspected to be extremely hazardous, the sample custodian supervisor is notified prior to the log-in process. The containers are opened by sample custodians who have successfully completed respirator fit-test and safety training sessions in the necessary protective equipment. The shipping containers are opened using all the safety measures deemed necessary by the Core safety consultant, if available, and the responsible supervisor.

Core sample receipt and log-in procedures are closely followed. The receipt of the sealed containers are documented on the appropriate chain of custody form. The persons authorized to open such containers will perform the log-in steps previously described in this section.

Subcontract Laboratory Chain of Custody

Samples are subcontracted by Core to approved laboratories for client required analyses that, for example, the Core laboratory does not regularly perform. Subcontract laboratory custody is documented on the Core Subcontract Chain of Custody form, Figure 7.8. For intercompany sample transfers, Figure 7.1 - 7.2 custody documentation may be used along with a completed Laboratory Analysis Request Log, Figure 7.9. Samples are shipped by Core using overnight carrier services, picked up daily by the subcontract laboratory or delivered by Core, depending on the subcontract laboratory utilized for the analyses.

Maintaining Internal Chain of Custody

Sample custody within the Core facility is documented on laboratory records by the sample custodians and the authorized Core personnel who take custody of the samples to perform the required preparation and analytical procedures. A number of internal custody records may exist for a sample for which multiple determinations are performed. Internal custody is established by the Core sample custodian.

Changes of custody within the laboratory are recorded on the Internal Custody Form, Figure 7.10, as they occur. The date and time that sample custody is assumed and relinquished is documented. Personnel signatures authenticate the accuracy of the information recorded on the form. The Appendix additionally includes Core laboratory chronicles for organic and inorganic preparations and analyses. The laboratory staff uses these documents, Figures 7.11 through 7.16, which offer further demonstration of internal custody while the samples are being worked on in the laboratory.

Sample Tracking

Sample preparation and analysis are documented through the use of laboratory chronicles and internal custody forms, as previously described. Computer reports generated from the LIMS show the status of each sample for every analysis, as updated by the responsible scheduler. Sample status information may be accessed electronically through the LIMS as well. LIMS generated sample hold time and turnaround reports are utilized by Core management to ensure that hold times are satisfied and client technical reports are completed on time.

When an analytical batch is completed, the transfer of the sample results from the analytical area to the technical report production area is recorded in a log notebook. The respective laboratory areas (cost centers) are updated in the LIMS for the change to the sample's status. When the technical reports are complete, a tracking system is utilized to mail the reports and archive them according to procedures identified in Section 10.

Sample Custody After Analysis

The laboratory custody of a sample routinely ends with laboratory disposal. Core's routine disposal of samples occurs after a minimum of thirty days from the mail date of the sample technical reports. Core retains samples for longer periods of time to comply with client or contract requirements, and returns remaining sample to clients at their request. At Core's discretion, hazardous samples may be returned to clients. Sample disposal is addressed at greater length in Section 9.0, Waste Disposal.

CALIBRATION PROCEDURES AND FREQUENCY

Instrument calibration is a mandatory requirement of performing quantitative analytical methodology. The laboratory must meet the established method criteria for instrument calibration and calibration verification before proceeding with sample analysis. Table 8.1 summarizes the laboratory's routine instrument calibration procedures.

Core will meet the calibration criteria specified in the methods. The analysts will not continue with an analysis or accept data unless the calibration requirements have been met. Likewise, when an analytical method or protocol includes the use of other instrument quality control procedures, such as GC/MS tuning, the analysis will not proceed unless the quality control criteria are met.

Analytical Reference Standards

Core's analytical reference standards are foundational to the quality of the analytical determinations performed. Instrument calibration and calibration verification is performed at the method required frequency utilizing analytical reference standards that satisfy the method or protocol specifications. Laboratory pure water and reagent grade or higher organic solvents and acids are used for solutions. Proper storage and handling techniques are followed. Standards are not used past their expiration dates.

Organic standards are obtained from a variety of vendors. Stock solutions or working calibration standards are prepared from purchased neat materials or concentrated solutions. Several custom working standards are purchased with the components at the desired concentrations. Core lot number designations can be used to trace reference standards to their purchased sources. Core's written documentation provides in-house traceability. Percent purity traceable to NIST and USEPA may be available from vendors. Vendor prepared standards utilized for several analytical protocol are purchased as certified by USEPA Contract Laboratory Program (CLP) procedures and criteria for analytical reference solutions.

Inorganic standards are obtained from vendors that specify traceability to NIST and USEPA materials. Most are purchased as solutions and diluted at the laboratory. Core's written documentation provides in-house traceability of the working reference solutions to their purchased sources. Lot numbers are used for several applications.

Both organic and inorganic standards preparations are thoroughly documented in laboratory notebooks or preprinted log sheets designated for that purpose. Preparation and expiration dates are indicated. The preparer signs, authenticating the laboratory entry. Recorded information includes: the concentrated source; the volume or weight of the source used in the dilution; the final volume and concentration level of the dilution; the acid, preservative or organic solvents used, etcetera. Dilution factors are recorded for several applications. Cross reference to other sources of information may be included in the documentation scheme. The preparation documentation is retained by the laboratory should it be needed for verification at a later date.

ANALYTICAL PROCEDURES

Methodologies

The Core laboratory utilizes approved USEPA methodologies for all analyses, if available and applicable. The deliverables included in the sample technical reports are based upon the level of report deliverable requested and the quality assurance requirements of the methods performed. Analytical results and quality assurance protocols are based upon, but not limited to, the following methods and guidelines.

"Methods of Organic Chemical Analysis of Municipal and Industrial Wastewater", Federal Register Vol. 49, No. 209, October 26, 1984;

"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 Third Edition, USEPA, September 1986 and Updates;

"Standard Methods for the Examination of Water and Wastewater", 17th & 18th Editions, American Public Health Assoc., American Water Works Assoc., Water Pollution Control Federation, 1989 and 1992;

"Methods for Chemical Analysis of Water and Wastes", EPA 600/4-79-020, EMSL, March 1983;

"Methods for the Determination of Organic Compounds in Drinking Water", EPA-600/4-88/039, EMSL, December 1988 with July 1991 revisions;

USEPA Contract Laboratory Program Statements of Work for Organics Analysis: SOW OLM01.0 and latest published revisions, 1990;

USEPA Contract Laboratory Program Statements of Work for Inorganic Analysis: SOW ILM02.1, September 1991; SOW ILM01.0 and latest published revisions, 1990;

"Handbook for Analytical Quality Control in Water and Wastewater Laboratories", EPA-600/4-79-019, March 1979;

National Enforcement Investigation Center Policies and Procedures Manual, EPA-330/9/78/001-R, Revised May 1986; and

"Emergency Standard Practice for Generation of Environmental Data Related to Waste Management Activities", ASTM ES 16-90, American Society for Testing and Materials, June 1990.

Core may revise procedures to reflect more recent method revisions or USEPA CLP Statements of Work (SOW) prior to or during a project, and reserves the right to utilize later method revisions or SOWs for project samples at that time.

Core has the capability of modifying methods, as well as performing specific client or project methods. Within normal laboratory operations, Core can design experiments or method improvements to offer its clients improved performance for a specified parameter.

Laboratory Glassware

The laboratory utilizes accepted procedures for cleaning laboratory glassware. Cleaning procedures differ based on the intended use of the glassware but always include washing in laboratory grade phosphate-free detergents, tap water rinses followed by deionized or other laboratory grade water rinse, and acid or solvent rinses or soaks as appropriate for the glassware's intended use.

After use, laboratory glassware is rinsed to remove contaminants prior to being placed in the glassware area for cleaning. Glassware is manually or machine washed according to specifications; all signs of visible discoloration and/or any materials that may have been present must be eliminated or the glassware is discarded. Glassware may be baked at a high temperature (400° C) to remove any potential residuals, depending on the piece and its intended use. Glassware is properly stored prior to use to ensure that contamination does not occur, and is solvent or acid rinsed as appropriate prior to use.

Materials Procurement and Control

Purchasing guidelines for all materials and performance guidelines for equipment having an effect on data quality are established. Materials are purchased according to method specifications or other regulatory or contract criteria; purchase order substitutions are not permitted by the purchasing department without prior expressed approval by authorized operations management.

Goods and materials are visually inspected upon receipt to ensure they are the items that were ordered from the vendor. Discrepancies are checked; materials that do not satisfy purity, quality or grade requirements are returned. Reagent lot number information are recorded on laboratory log sheets; clean method blanks indicate that reagents utilized for an analytical determination did not contribute to the presence of an analyte in a sample.

Chemicals and reagents are stored in accordance with applicable fire and safety regulations and guidelines, protocol requirements and under conditions specific to the material or its use. Areas dedicated for chemical reagent storage are well maintained and orderly; materials maintained by bench personnel are expected to be inventoried and stored in a similar manner.

The laboratory realizes the importance of proper storage and documentation procedures for both analytical reference standards and chemical reagents. Chemicals and reagents arriving at the facilities in vendor shipments are dated upon receipt to establish their order of use and minimize the possibility of exceeding their useful shelf life. Likewise, analysts and technicians are trained to date materials upon opening as a tracking mechanism for the material.

Periodically, inventories are reviewed and materials are evaluated for disposal. Materials that are received without a manufacturer's expiration date are assessed based upon receipt and opening dates and the nature of the material. When contamination is traced to a reagent, the bottle or entire lot is removed from service.

Core Reagent Grade Water

Core maintains several water purification systems within the laboratory that produce water of sufficient quality so as to be demonstrated acceptable for use in preparation of reagents and method blanks, and provided for sampling activities as field, trip, equipment and rinsate blanks. The same source waters that are used for ongoing laboratory analyses are provided for client use. Blanks that are provided to clients in sample shuttles must be prepared on the day that the shuttle is shipped from Core. The water is monitored daily for specific conductance.

The Core water purification system includes a reverse osmosis process incorporating carbon and deionizing tanks prior to the end use. Dependent upon the use, additional prefilters, carbon tanks, deionizing tanks and organic scavenger polishers may be used on the finished water. Core water purification processes also include independent tank systems that are configured to generate a finished water suitable for its intended laboratory use.

Waste Disposal

Core's waste disposal practices conform to all USEPA and NJDEP waste handling requirements. The laboratory retains a RCRA Part A permit (generator only) which allows the laboratory to generate and store hazardous materials for a maximum of ninety days. Wastes are shipped to USEPA permitted and approved treatment, storage, and disposal facilities prior to expiration of the ninety day limit. Core performs a bulk reduction step which destroys sample bottles and labels; consequently, a sample cannot be identified in the waste at a later time.

Before engaging a waste disposal firm, Core obtains copies of the firm's permits and all applicable identification numbers. The firm must provide certificates of insurance to demonstrate adequate liability coverage. Waste disposal firm information is updated on an annual basis. Core maintains records on all waste transactions and waste contractor documentation. Waste manifests are processed as required.

Laboratory wastes are segregated into several waste streams. Aqueous wastes are treated as a single stream and removed to a waste treatment plant by a bulk handler. Solid material is segregated into soils/sludges and solid laboratory trash (not sample related), and removed to a subtitle C waste facility. PCB containing wastes (samples with known amounts or sample extracts containing PCBs) are removed to facilities permitted to accept TSCA wastes. Samples containing Polychlorinated Dibenzo-p-Dioxins are isolated and returned to the client (or, alternatively, may be disposed of through a USEPA approved pathway). Oil/water mixtures and waste solvents are sent to a USEPA approved fuel blending facility.

DATA REDUCTION, VALIDATION AND REPORTING

Data reduction, validation and reporting describes the processes that result in the delivery of quantitative analytical data to the data user. These processes include calculation of raw data into final concentration units, reviewing results for accuracy and assembly of the technical report contents for delivery to the data user. The following describes procedures employed at Core for translating raw analytical data into accurate, finished sample reports and data storage.

Data Review and Processing Procedures

All organic and inorganic data generated by Core are reviewed by designated trained personnel. The analysts who acquire the data are responsible for initial on-line checks for compliance to the analytical requirements. After a sample batch is acquired, the data review procedure includes data interpretation and quantitation, inspection of quality control data against criteria, data reduction, narrative or comments writing, and ensuring that the data package includes all required analytical and quality control results, raw data and laboratory chronicles. After review and acceptance, analytical results are processed or entered into Core's computerized data base and tabular summary tables are generated, or USEPA CLP forms are created.

The completed data package is transferred to a designated reviewer who performs a quality control audit for use of the proper methodology and detection limits, compliance to quality control protocol and criteria, presence and completeness of required deliverables, and accuracy of calculations and data quantitation.

Data packages are then transferred to the production service personnel who review each data package to ensure compliance with client orders by reviewing on-line input in the Core computer tracking system. The laboratory data is assembled in the client's technical reports. Reports are reviewed for completion prior to reproduction in the copy/bind department. Figure 10.1 gives an overall view of the general operations flow.

Use of checklists ensure that all data is systematically handled and no steps are omitted. Checklists are reviewed, and are retained and accessible should they need to be referenced at a later date. The data and deliverables are checked and signed during processing procedures, and then systematically filed by reference identification numbers.

Technical Report Deliverables

Technical reports are prepared to include the components or level of deliverables that are requested by clients for samples or projects, or contractually required. Core's standard report includes tabular results, data system printouts for several analyses, chain of custody records, and, as provided to the laboratory, sampling time and date, field location codes and client sample point identifications. Quality control results are routinely included for several analyses.

Core also prepares technical reports that include full data deliverables for validation purposes, and lesser, abbreviated reports. Full deliverables include all raw and processed data applicable to the analyses performed. Core prepares single sample technical reports or multi-sample report packages. The multi-sample technical reports contain results for a sample delivery group (SDG) or other client or laboratory defined sample set. Core recommends multi-sample reports when full deliverables packages are required.

The Core laboratory prepares electronic data deliverables as required for contracts and upon client request.

Data Archive

Sufficient records are retained to recreate analytical events at the laboratory. Records are cataloged and maintained in limited access areas. Data archive and storage is managed by designated individuals who control the access to stored information.

All information retained at the Core facility is stored in secured areas. All hard-copy information is stored on-site at the laboratory or off-site at a commercial document storage facility equipped with a professional security system. All electronic data is stored on-site at the laboratory or off-site at a commercial document storage facility equipped with a professional security system and a controlled environment suitable for storage of magnetic media.

Core reserves the right to transfer hard-copy information onto microfilm. Core reserves the right to store information in hard-copy files, on magnetic media and/or microfilm. The information is retained and accessible for a minimum of seven years unless otherwise specified through a client specific contract.

Response to Inquiries

The Core laboratory recognizes the importance of its timely response to inquiries regarding the laboratory's work for samples and projects. The laboratory will respond to inquiries as rapidly as possible as part of its corrective action plan. Core should be considered the primary contact for all data inquiries when subcontract or other network laboratories are used for analyses.

INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

The responsibility for the internal analytical quality control checks rests with the laboratory analyst. The type, frequency and acceptance criteria of the checks performed are based upon the reference analytical methodology employed and client or project requirements. In cases where the project required method does not address these critical issues, Core may recommend that quality control protocols be established on a per method basis to meet the intended data quality objectives of the project.

The following descriptions present a summary of quality control samples that are used routinely for Core projects. These data are compiled and are used both by the QA department and project staff to monitor data for systematic analytical problems.

Trip Blank: Analyte free reagent grade water prepared by the laboratory, shipped in the Sample Shuttle, and analyzed with the samples to detect accidental or incidental contamination during transport. Analyzed as required for a project.

Field Blank: Reagent grade water provided by the laboratory that is transferred on-site to an additional clean sample container to evaluate the environmental or procedural effects of a sampling event; used to determine if contamination occurred during field sampling. Analyzed as required for a project.

Equipment Blank (Rinsate Blank): Reagent grade water provided by the laboratory that is passed through sampling equipment to determine the effectiveness of the field equipment cleaning procedures. Analyzed as required for a project.

Method Blank (Reagent Blank): A blank used to check chemical reagent or process introduced contamination in the laboratory. Analyzed, at minimum, at a 1:20 sample frequency or as required by a method if more often.

Quality Control Spiked Blank/Laboratory Control Sample: Secondary/independent source standard reference materials spiked into reagent grade water or other blank material and carried through the entire preparation and/or analytical process to verify or demonstrate method performance. Analyzed, at minimum, at a 1:20 sample frequency or as required by a method if more often.

Spiked Sample (Matrix Spike): A client sample spiked with standard reference materials and carried through the entire preparation and/or analytical process to evaluate sample matrix effects on analyte recovery and accuracy. Analyzed, at minimum, at a 1:20 sample frequency.

Unspiked Laboratory Duplicate: A client sample which is split and carried through the entire preparation and/or analytical process as a replicate sample to evaluate laboratory reproducibility and precision. Analyzed, at minimum, at a 1:20 sample frequency for metals and wet chemistry determinations.

Spiked Laboratory Duplicates (Matrix Spike & Matrix Spike Duplicate): A client sample which is split, spiked with standard reference materials, and carried through the entire preparation and/or analytical process as a replicate sample to evaluate sample matrix effects on analyte recovery and accuracy as well as laboratory reproducibility and precision. Analyzed, at minimum, at a 1:20 sample frequency for organics determinations.

The following are added to field and quality control samples for organic analyses:

Internal Standards: Compounds that possess similar chemical and physical properties to the target analytes. Added to samples or extracts prior to analysis, and used as retention and response reference points and to verify instrument performance. Evaluated as specified in the applicable GC/MS analytical methods. Used for several GC determinations.

Surrogates: Compounds that possess similar chemical and physical properties to the target analytes. Added to each sample to check for matrix effects or other difficulties related to method application. USEPA CLP and SW-846 recommended surrogates and recovery limits are used and reported when available.

PERFORMANCE AND SYSTEM AUDITS

Internal and external performance and system audits are used to assess the laboratory's ability to perform and support environmental analyses by evaluating it against required protocol or other stated objectives. Outlier values and investigative findings can result in corrective actions that are designed to cause improvement and prevent recurrences or lead to, for example, conformance to a specific future project's requirements.

A performance audit is a quantitative or qualitative evaluation of analytical data produced by a laboratory using samples containing analytes of interest. Performance audit samples, known also as proficiency or performance evaluation samples, are introduced to the laboratory as single or double "blinds", referring to the amount of information the receiving party is told in advance about them. With single blinds, the laboratory knows that the samples are for audit purposes but does not know the analytes and/or the concentrations present. With double blinds, the laboratory does not know that the samples are audit samples. Typical performance audits provide the means to assess precision and accuracy, as well as analyte identification.

A systems audit is an inspection and review of the data generation, quality control and support system of an analytical laboratory. This inspection and compliance review includes all activities related to the requirements established for the laboratory quality assurance program. Typical systems audit include an evaluation of the following:

- Assessment of degree of compliance with the quality assurance program including certification programs, SOP completeness, completeness of quality assurance project plans, assessment of QA documentation, data review and approval process, internal QC program, and internal audits;
- Continuing compliance with corrective actions identified in a previous audit of the facility;
- Detailed performance audits of selected analytical programs;
- Calibration procedures and documentation;
- Sample handling procedures including chain of custody; and
- Experience of laboratory personnel.

Internal Audits

The Core quality assurance staff conducts scheduled and unscheduled audits that are designed to aid in the fulfillment of quality assurance objectives within the facility. Good laboratory practices, safety and conformance to standard operating procedures and methodologies, as well as results of internal performance audit samples, are reviewed by the QA staff. Systems audits are scheduled on a bimonthly basis.

Reports may be submitted to the area managers and laboratory director when non-conformances are observed, or other follow-up is taken. The responsible area managers are accountable for the timely implementation of the corrective actions. Unscheduled audits are conducted to confirm that critical concerns have been addressed. Corrective actions are monitored. Internal audit reports are confidential to Core employees.

External Audits

Clients and regulatory agencies routinely audit the Core facility. The audits include performance evaluation samples submitted as blinds or double blinds for analysis, as well as announced and unannounced on-site laboratory inspections. The QA staff hosts or otherwise participates in external systems audits, which occur frequently on an ongoing basis. The external audit schedule is variable based upon client and regulatory requirements.

The laboratory participates in a number of ongoing, scheduled performance audit activities. Core participates twice yearly in USEPA Water Supply (WS) and Water Pollution (WP) performance evaluation studies, quarterly in proficiency studies from the State of New York (two potable water and two non-potable water/solid/hazardous waste studies per year), annually in USEPA Discharge Monitoring (DM) studies, annually in limited studies from the State of Wisconsin, and, when scheduled, solid and hazardous waste studies from the State of California. United States Army Corps of Engineers (USACE) proficiency samples, required for initial and continued validation, are analyzed, at minimum, every eighteen months. In addition, Core analyzes proficiency samples annually, or any other client-defined frequency, for private sector clients. Core analyzes external performance evaluation samples to support the environmental laboratory certification programs described below and private sector client laboratory approval programs and contracts.

Core is regularly audited by state agencies for compliance to state certification regulations. Private sector laboratory approval programs also include periodic laboratory audits. Projects and contracts frequently require laboratory inspection prior to award and at designated intervals thereafter. Core management is responsible for responding to the findings of external audits using the same mechanisms employed for internal audits, and for implementing corrective actions.

Certifications and Approvals

Core participates in a number of environmental laboratory certification and approval programs. Approval entails laboratory evaluation which includes, but is not limited to, representative proficiency samples, initial and periodic systems audits, and other proof of laboratory qualification.

Core holds or will obtain the appropriate state certification for every active project requiring analysis by a state certified environmental laboratory. Core currently participates in eleven state certification programs and is approved for the analysis of drinking waters, non-potable waters and solid/hazardous wastes. The types of certification available to environmental laboratories varies from state to state. Refer to Table 12.1 for Core's state certification list, certification numbers and the types of approval held.

Core is also approved by federal Department of Defense (DOD) environmental laboratory approval programs. Core is validated by the United States Army Corp of Engineers (USACE) Missouri River Division (MRD) and is Naval Energy and Environmental Support Activity (NEESA) Installation Restoration Program (IRP) approved.

Data Quality

The Core laboratory maintains records of the quality control data generated for analytical batches, including, but not limited to, method blank, spiked blank recovery, spiked sample recovery, duplicate sample, and surrogate recovery data. The data may be used to statistically determine or assess precision, accuracy, method validity and process control, and monitor performance for corrective action.

Core administers a program designed to investigate and resolve internal and external data challenges. The goal is to ensure that the issues, investigations and resolutions are documented and tracked. The overall system, particularly the self-inspection aspect, enables Core to develop strategies and policies to reduce any systematic errors.

PREVENTATIVE MAINTENANCE PROCEDURES

Core, being a highly computerized and instrument oriented laboratory, maintains service contracts for major instruments for routine maintenance and emergency call service. Service engineer support for other instrumentation is available and utilized on a scheduled or as need basis. Core performs routine maintenance to prevent instrument malfunction and minimize downtime, and to optimize instrument capabilities.

In the event of an instrument breakdown, several options may be considered while service is being performed. Core may schedule the work on another instrument, request the vender to provide another instrument, or subcontract the work to an approved subcontract laboratory or Core Laboratories, Inc. location, providing certification requirements are satisfied and the client consents.

Preventative Maintenance

Analysts are trained to respond to instrument maintenance needs. Criteria for this type of maintenance is based on instrument performance. Failure of instruments to perform according to stated methodologies and criteria limits drives the need for daily maintenance. The schedule of preventative or routine maintenance checks are, in general, outlined within the specific equipments' operators manuals and in the analytical procedures performed. Core adheres to these schedules, and it is the responsibility of both the analyst and department manager to ensure these checks are completed.

Replacement Parts

The laboratory maintains an inventory of replacement parts for all analytical instrumentation. This enables Core analysts to perform routine maintenance and repair of instruments as needed.

Record keeping and Preventative Maintenance Logbooks

Instrument specific logbooks are utilized to record instrument problems, maintenance and demonstration of control. Core maintains one current logbook per instrument. Analysts are required to record all maintenance performed on an instrument; outside service engineer records are included so the maintenance documentation is complete. If an instrument is unusable, a label stating so is placed on the instrument to avoid its use.

Thermometers, Refrigerators, Ovens and Balances

Laboratory thermometers are calibrated against NIST traceable thermometers annually. The results are recorded in a logbook specific to that purpose. Correction factors are recorded on the thermometer tags, along with the unique thermometer identification number and calibration date, and used by Core personnel to correct actual temperature measurements. The correction factor is applied to each reading until the thermometer is calibrated again. Use of thermometers with a correction of > 5° C is avoided. Core minimizes the need to apply corrections by utilizing the correct media, thermometers and procedures during calibration.

Refrigerators and ovens are monitored once or twice daily or as used, dependent upon the function of the unit. Logbooks are maintained by the units to record monitoring and results. If a unit fails acceptance criteria, monitoring is continued until the temperature stabilizes within the range or appropriate corrective actions are taken. Monitoring occurs at one (1) hour intervals for a maximum four (4) hour period; if the reading following the temperature control adjustment is out, the unit is considered "out of order", and is emptied and serviced. It is not put back into service until shown to be stable at the required temperature range.

Analytical balances are calibrated annually by an outside service. A dated sticker, certifying the calibration, is placed on each balance. Records for balance calibration and servicing are maintained in Core QA files. Multiple and single point calibration checks are regularly performed to ensure the accuracy of each balance. The results are recorded in dedicated logbooks that are maintained at each balance location. Balances that do not satisfy specifications are taken out of service for replacement or repair.

SPECIFIC ROUTINE PROCEDURES TO ASSESS DATA PRECISION AND ACCURACY

For every batch of samples analyzed, a series of quality control samples are analyzed to assess the precision, accuracy and validity of the analysis. These data are reviewed before release of the data. All QC data are stored at Core and are useable for determination of method precision and accuracy. Core makes every effort to meet or exceed the accuracy and precision data as defined within specific methodologies. However, for actual matrices these data may not be comparable. If no precision or accuracy requirements are specified within a methodology, Core will establish criteria, and maintain the quality control limits for valid method use.

Accuracy is characterized by the degree of agreement of a measured value to the accepted true value. Data comparability is a fundamental underlying assumption to all accuracy assessments. Accuracy assessments are used to establish the bias present in the data. Precision is characterized by the degree of agreement of a measured value to another measured value. Data comparability is a fundamental underlying assumption to all precision assessments. Precision assessments are used to establish the control status of a system, such as a sampling process or a measurement process.

Completeness is characterized by the degree of agreement of the quality of a data set to the method and/or client specification. Completeness is defined as the percentage of measurements made which are judged to be valid measurements. The completeness goal is to generate a sufficient amount of valid data based on project needs. Comparability of the quality control data model to the experimental data set is a fundamental assumption to all completeness assessments. Comparability is a measure of the confidence with which one data set can be compared to another data set. Completeness assessments are used to characterize the applicability of the data.

To estimate accuracy, spiked blank samples and matrix spike sample recoveries are evaluated. This allows for the determination of both method and actual sample batch accuracy. Precision is measured and monitored in two ways: using range control for duplicate pairs and relative percent difference. Core uses the formulas presented in Standard Methods and the USEPA Quality Assurance handbooks for calculations of precision and accuracy.

Accuracy Control

The objective of the laboratory concerning accuracy is to meet or exceed the accuracy criteria specified in an analytical method. Accuracy determinations are performed for each parameter according to the specifications of the particular method employed. Accuracy assessments are performed by the analysts via a first level data review. The analysts will compare data results to the established acceptance criteria. When the criteria is not met additional characterization of the data is required according to the requirements of the methodology and as determined by the judgement of the analyst in order to establish the accuracy of the data.

For each type of spiked sample accuracy control charts are developed. Control limits are established according to the requirements of the methodology. In the absence of published control criteria the limits are calculated. The limits are calculated based on the mean and standard deviation of a pooled data set. The data set must contain of no less than seven (7) data results. Limits are then calculated.

Precision Control

The objective of the laboratory concerning precision is to meet or exceed the criteria specified in an analytical methodology. Precision measurements are performed for each parameter according to the specifications of the particular method employed. Precision assessments are performed by the analysts via a first level data review. The analysts will compare data results to the established acceptance criteria. When the criteria is not met then additional characterization of the data is required according to the requirements of the methodology and as determined by the judgement of the analyst in order to establish the precision of the data.

For each type of replicate sample and MS/MSD pair, precision control charts are developed. An upper control limit is established according to the requirements of methodology. In the absence of published control criteria, the limit is established as 20 percent.

Calculations To Determine Accuracy

Accuracy is calculated as follows.

$$\% \text{ Recovery} = \frac{(X - T)}{K} \times 100$$

where:

K	Known addition of the spiked compound
X	Analytical result from the spiked sample
T	Analytical result from the unspiked aliquot

Standard deviation (Sp) is used for determining the variation among several recovery samples, and establish upper and lower warning and control limits. Standard deviation is calculated as follows.

$$Sp = \text{the square root of } \frac{(X - \bar{X})^2}{(n - 1)}$$

where:

Sp	Standard deviation of % Recovery
$\underline{X}$	Observed value
X	Mean or average of all observations
n	Number of observations

Control limits are created to determine the acceptable range of analyte recovery and are used to compare actual spike recovery results against. Control limits are calculated as follows.

$$UCL = \bar{X} + 3\ Sp$$

$$LCL = \bar{X} - 3\ Sp$$

$$UWL = \bar{X} + 2\ Sp$$

$$LWL = \bar{X} - 2\ Sp$$

where:

$\bar{X}$	Average Value
Sp	Standard Deviation
UCL	Upper Control Limit
LCL	Lower Control Limit
UWL	Upper Warning Limit
LWL	Lower Warning Limit

Calculations To Determine Precision

The precision of duplicate sample pairs is expressed as Relative Percent Difference (RPD) and is calculated as follows.

Relative Percent Difference

$$RPD = \frac{|A - B|}{(A + B)/2} \times 100$$

where:

RPD	Relative Percent Difference
A	Replicate value 1
B	Replicate value 2

Standard deviation can be used to determine variation among several RPD values for duplicate pairs and establish statistical limits for duplicate RPD. Standard deviation and control limit calculations are shown in the above discussion of accuracy. Range control may also be used.

Range Control

$$R = A - B$$

$$\bar{X} = \frac{A + B}{n}$$

where:

R	Range of a pair of results
X	Average of a pair of results
A	Duplicate value 1
B	Duplicate value 2
n	n = 2 represents a single duplicate pair

To graphically represent the data of numerous duplicate pairs on control charts, the following calculations are performed using statistical numbers.

$$\bar{\bar{X}} = \text{the sum of } \bar{X} / n$$

$$\bar{R} = \text{the sum of } R / n$$

where:	$\underline{\bar{\bar{X}}}$	Grand Mean
	$\underline{\bar{R}}$	Average Range
	X	Average of a pair of results
	R	Range of a pair of results
	n	n = 2 represents a single duplicate pair

Control limits for ranges (R - bar chart):

$$CL = 3.27\ (\bar{R})$$

$$WL = \bar{R} \pm 2/3\ (3.27\ \bar{R} - \bar{R})$$

where:	$\bar{R}$	Average Range
	CL	Control Limit
	WL	Warning Limit

To determine if the proper range control chart is being used for evaluation of a duplicate pair of results, the X control chart may be used.

Control limits for averages (X - bar chart):

$$UCL = \bar{\bar{X}} + 1.88\ (\bar{R})$$

$$LCL = \bar{\bar{X}} - 1.88\ (\bar{R})$$

$$UWL = \bar{\bar{X}} + 2/3\ (1.88\ \bar{R})$$

$$LWL = \bar{\bar{X}} - 2/3\ (1.88\ \bar{R})$$

where:	$\underline{\bar{\bar{X}}}$	Grand Mean
	R	Mean Range
	UCL	Upper Control Limit
	LCL	Lower Control Limit
	UWL	Upper Warning Limit
	LWL	Lower Warning Limit

Standard deviation provides the basis for the determination of precision from pooled spiked sample accuracy data. This precision determination may be used to establish control limits as described in the accuracy discussion above.

<u>Calculation To Determine Completeness</u>

The percent completeness obtained for a data set is calculated as follows.

$$\%\ \text{Completeness} = \frac{\text{Number of control parameters that satisfy criteria}}{\text{Total number of control parameters}} \times 100$$

CORRECTIVE ACTION

Corrective action is defined as those actions necessary to place any operational process or analytical system back into its performance specification. It is the objective of the laboratory to implement appropriate corrective action when and where necessary in an effective and timely manner.

When a situation or issue is identified that requires a corrective action, it is investigated and evaluated using processes that address the requirements for the specific nonconformance found. In a case where there is a lack of existing requirements that may be applied, identification of the requirements is included in the corrective action plan.

The corrective action is identified and documented through one of several internal report processes. The Investigation/Correction Log, Figure 13.1, is utilized for internal and external issues, client and agency inquiries, performance and systems audits, and other non-routine occurrences, findings or recognized needs. A Routine Corrective Action Log, Figure 13.2, is produced for every batch of analytical samples and used by the technical staff prior to reporting sample data. The form is used to document routine analytical problems and return-to-control following corrective action activities described in the methods and Core SOPs.

In the event that any corrective actions are needed because the data quality is in question above and beyond those actions stipulated in the analytical methods, the client will be contacted by Core to discuss the problem.

Corrective actions are initiated at all operational levels within the laboratory, involving analysts, their management, and the quality assurance group in both formal and informal procedures. Analysts are responsible for taking routine informal corrective actions described in the methods. Corrective actions are also initiated externally through project management personnel in local, state, or federal agencies and private sector clients. In each case, after an assessment of the issue, appropriate steps are taken to correct the situation and prevent it from occurring again.

Depending on the severity, corrective actions may be taken at the analyst level, department level, or within the entire laboratory. Core recognizes the importance of corrective action to maintain a high quality program. In this light, data are reviewed for completeness, accuracy, precision and compliance with analytical method quality control and project specifications during the data generation and reporting process.

Specific corrective action responses are performed for quality assurance/quality control deficiencies; many are pre-defined in the analytical protocol used for the samples. In general, there are three major types of corrective actions which are initiated at Core.

<u>To correct sample problems:</u> Individual samples or matrix problems are usually handled within the analytical laboratory. Corrective actions may include repreparation and re-analysis, clean-ups, dilutions or matrix modifications. All actions taken are documented with the analytical results.

A typical example is when organic surrogate compound recoveries are outside of the acceptance limits; if no calculation or other problems are found, the sample is routinely reprepared/reanalyzed to verify matrix effects. Every effort is made to meet sample hold times.

<u>To correct sample batch problems:</u> An entire batch of samples may require corrective action if quality control criteria are not met. Laboratory managers are involved in the decisions for actions which may include re-analysis, re-extraction, etc. The quality assurance staff may review both sets of data as applicable to determine if the problems have been resolved.

A typical example is when method blank contamination occurs; if analytes are confirmed present at unacceptable levels, the batch is routinely reprepared/reanalyzed after the source of contamination has been identified and eliminated. Every effort is made to meet sample hold times.

<u>To correct systematic problems:</u> Those problems of a procedural nature are handled by the laboratory managers and quality assurance group. Major operational changes are made only after approval by appropriate Core management.

Systematic problems are identified as repetitive in nature or involving a number of samples or batches. Procedures involving analyst technique or training, or use of defective equipment or materials are identified and corrected.

QUALITY ASSURANCE REPORTS TO MANAGEMENT

An objective of the Core quality assurance program is to ensure that an operational system is in place which enables management to determine the quality level of all data produced within the laboratory system. An essential component of the system is the communication pathways and feedback mechanisms which insure that management obtains quality information promptly and consistently. To achieve this objective, Core employs informal and formal reporting processes to ensure that management is informed of operational quality. This information enables Core to take corrective action promptly when required. Reporting occurs at the following frequency:

- Daily meetings to discuss possible quality assurance problems and proposed solutions.

- Minimum weekly meeting with upper management to discuss laboratory performance, upcoming audits, certification, and past audit performance.

- Monthly written reports to the Quality Assurance Director, Core Laboratories, Inc. to provide detailed information on specific quality and laboratory issues. Copies are to be submitted to the Laboratory Manager, Regional Manager and Division Vice President, as well.

- As required for audits, written reports with observations and suggested corrective action procedures.

APPENDIX -

FIGURES AND TABLES

CORE LAB

Figure 1.1

ENVIRONMENTAL & PETROLEUM TESTING SERVICES

LOCATIONS DIRECTORY

United States

California

Anaheim
1250 E.Gene Autry Way
Anaheim, CA 92805
Phone: (714)937-1094
Fax: (714)937-1170

Long Beach
3700 Cherry Avenue
Long Beach, CA 90807
Phone: (310)595-8401
Fax: (310)427-5174

Colorado

Aurora
10703 East Bethany Drive
Aurora, CO 80014
Phone: (303)751-1780
Fax: (303)751-1784

Florida

Tampa
5460 Beaumont Center Blvd.
Tampa, FL 33634
Phone: (813)884-8268
Fax: (813)885-4938

Indiana

Indianapolis
7726 Moller Road
Indianapolis, IN 46268
Phone: (317)875-5894
Fax: (317)872-6189

Indiana (cont)

Valparaiso
2400 Cumberland Drive
Valparaiso, IN 46383
Phone: (219)464-2389
Fax: (219)462-2953

Louisiana

Lafayette (Sales Office)
111 Rue Jean Lafitte, Suite 103-B
Lafayette, LA 70508
Phone: (318)235-9431
Fax: (318)237-7053

Lake Charles
3645 Beglis Parkway
Sulphur, LA 70663
Phone: (318)583-4926
Fax: (318)583-4929

New Jersey

Edison
284 Raritan Center Parkway
Edison, NJ 08837
Phone: (908)225-6700
Fax: (908)225-6777

Texas

Carrollton (Sales Office)
1875 Monetary Drive
Carrollton, TX 75006
Phone: (214)466-2673
Fax: (214)323-3930

Texas (cont)

Corpus Christi
1733 North Padre Island Drive
Corpus Christi, TX 78408
Phone: (512)289-2673
Fax: (512)289-2471

Houston (Corporate Office)
5295 Hollister Road
Houston, TX 77040
Phone: (713)460-9600
Fax: (713)690-3947

Houston (Petroleum)
8210 Mosley Road
Houston, TX 77075
Phone: (713)943-9776
Fax: (713)943-3846

Houston (Environmental)
6310 Rothway Drive
Houston, TX 77040
Phone: (713)690-4444
Fax: (713)690-5646

San Antonio (Sales Office)
510 E. Ramsey, Suite 2
San Antonio, TX 78216
Phone: (210)344-9751
Fax: (210)344-6485

Wyoming

Casper
420 West First Street
Casper, WY 82601
Phone: (307)235-5741
Fax: (307)266-1676

International

Canada

Calgary
1540 25th Avenue, N.E.
Calgary T2E 7R2
Phone: (403)250-4000
Fax: (403)250-5120

Indonesia

Jakarta
Bldg. 303, Cilandak Commercial Estate
Jalan Cilandak K.K.O.
Jakarta, Selatan, Indonesia 12560
Phone: (62-21)780-1533
Fax: (62-21)780-2042

Malaysia

Kuala Lumpur
No. 17, Jalan U1/23, Section U1
HICOM, Glenmarie Industrial Park
Shah Alam, Selangor Darul Ehsan
Malaysia 40000
Phone: (60-3)705-1188
Fax: (60-3)705-2288

Scotland

Aberdeen
Kirkhill Industrial Estate
Howe Moss Drive
Dyce, Aberdeen, Scotland AB2 0ES
Phone: (44-1224)723303
Fax: (44-1224)770168

Venezuela

Maracaibo
Calle 25, Carretera Via el Mojan
Parcelamiento Buena Vista
Apartado 116, Maracaibo
Estado Zulia, Venezuela
Phone: (58-61)415020
Fax: (58-61)910611

Figure 4.1

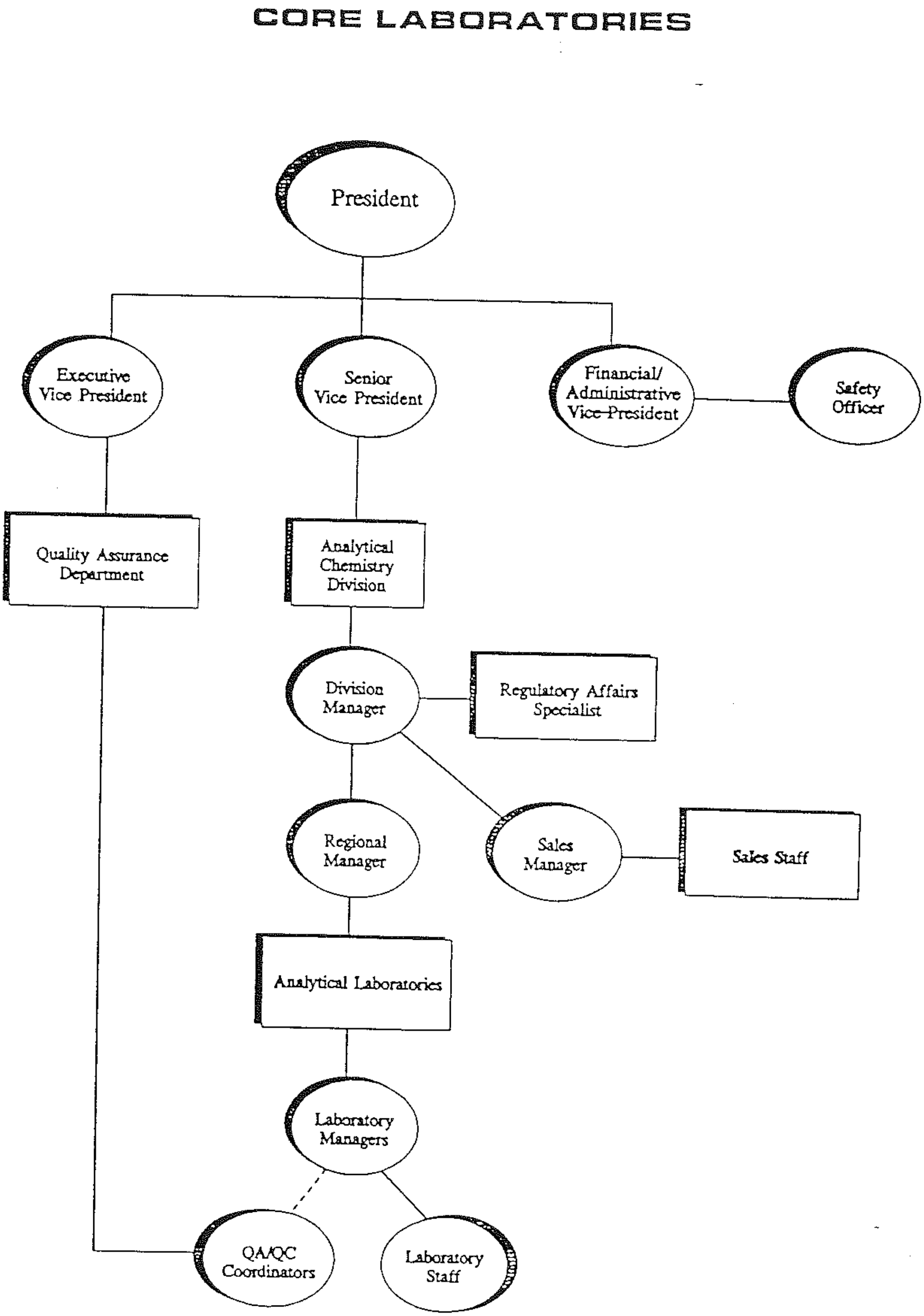
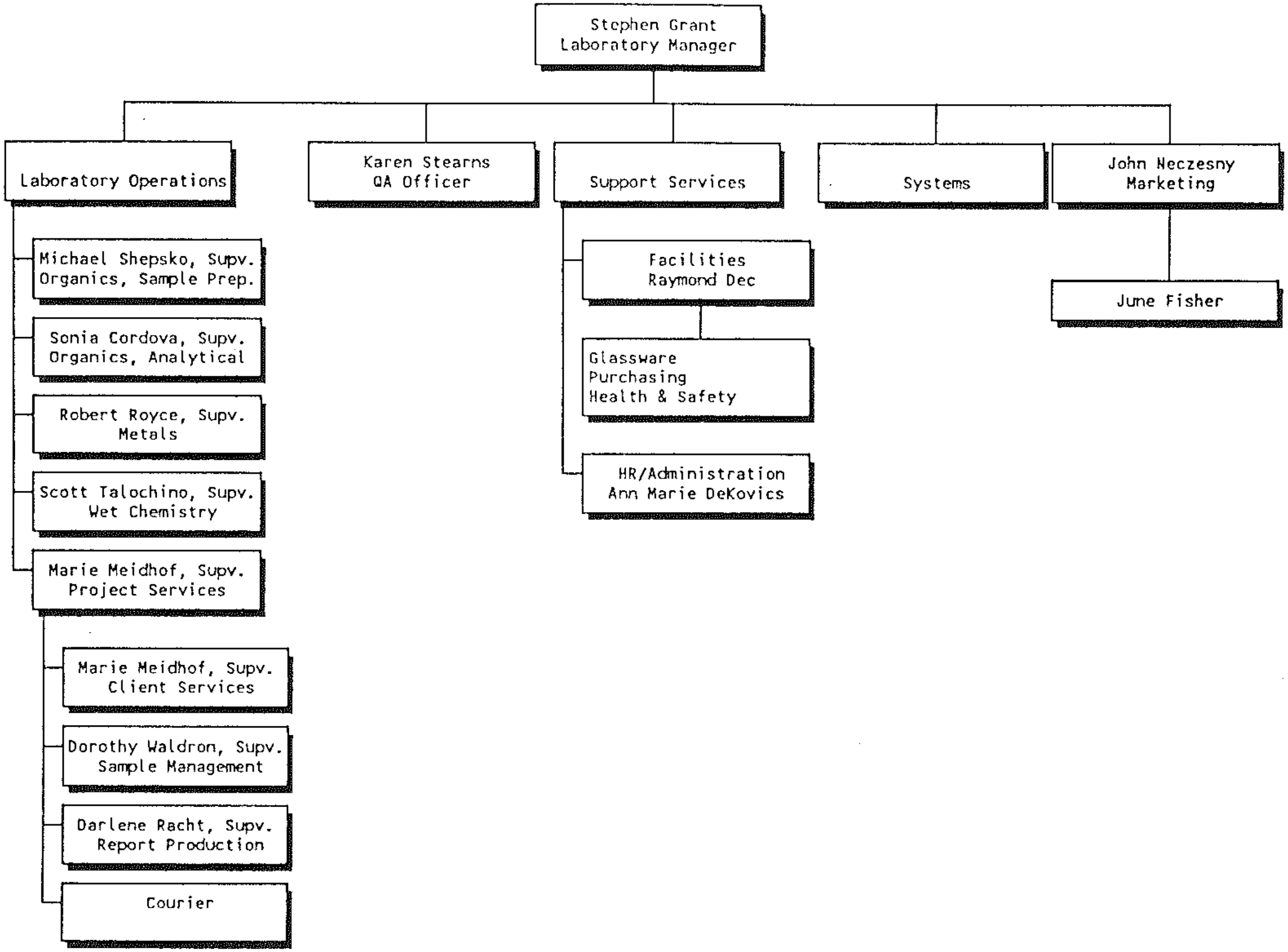

CORE LABORATORIES
President
Executive Vice President
Senior Vice President
Financial/ Administrative Vice-President
Safety Officer
Quality Assurance Department
Analytical Chemistry Division
Division Manager
Regulatory Affairs Specialist
Regional Manager
Sales Manager
Sales Staff
Analytical Laboratories
Laboratory Managers
QA/QC Coordinators
Laboratory Staff

Figure 4.2

This Quality Assurance Plan (QAP) is document controlled. The figure in place at the time of approval and a current chart are included in order to provide updated laboratory information.

CORE L[illegible]ATORIES
EDISON, NJ FACILITY
FEBRUARY 1996



CORE LABORATORIES
EDISON, NJ FACILITY
JANUARY 1996

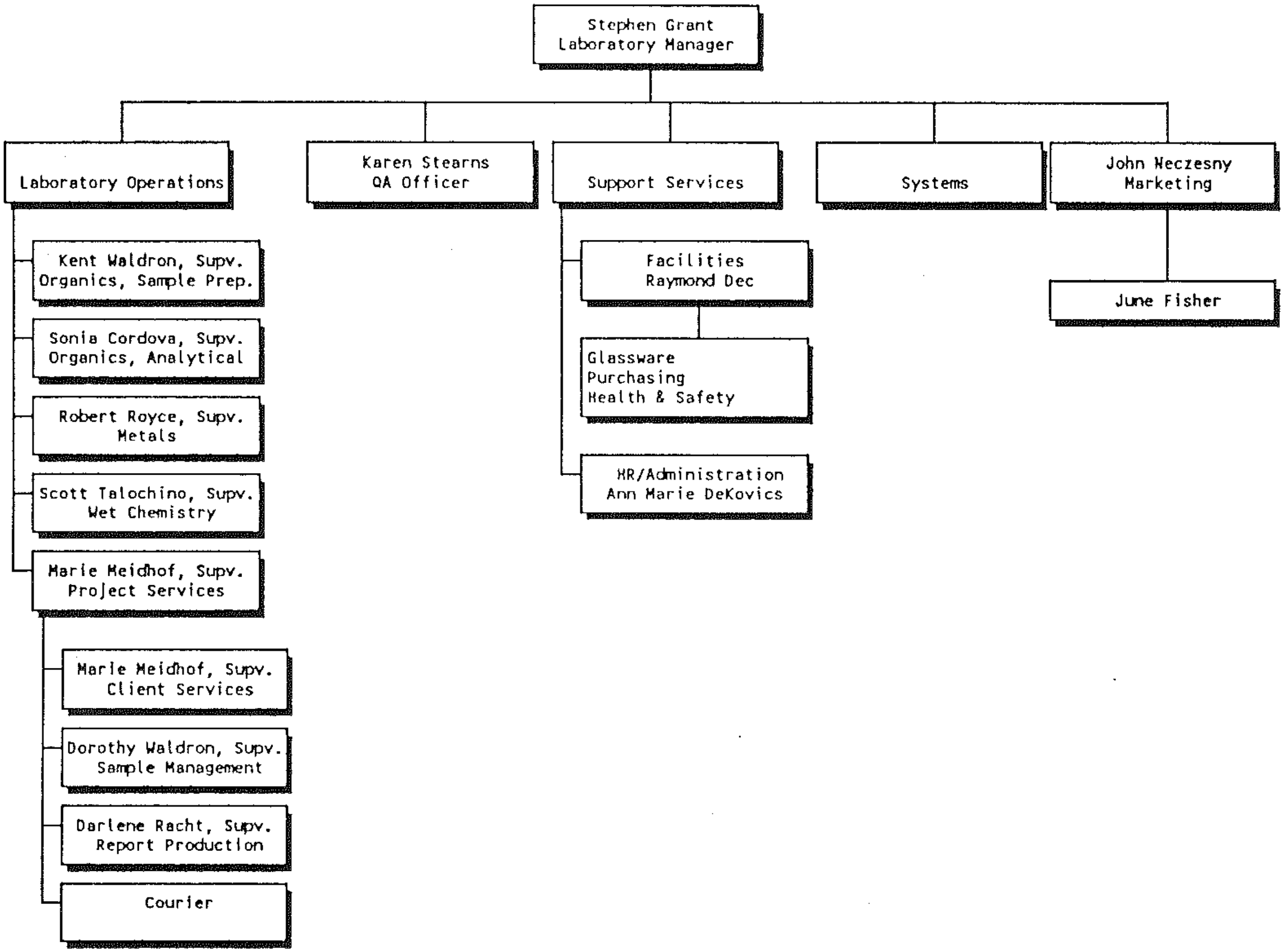


Figure 4.2

Figure 4.3 Project Organization - Core Personnel

Title	Name
Account Executive	*
Project Manager	*
Laboratory Manager	Stephen R. Grant
Quality Assurance Officer	Karen M. Stearns

* Personnel are named in project-specific quality assurance plans.

Table 5.1 Core Matrix Spike Percent Recovery Limits

Fraction	Parameter	Water	Soil
Volatile Organics by GC/MS			
VOA	1,1-Dichloroethene	61-145	59-172
VOA	Trichloroethene	71-120	62-137
VOA	Chlorobenzene	75-130	60-133
VOA	Toluene	76-125	59-139
VOA	Benzene	76-127	66-142
Extractable Organics by GC/MS			
BN	1,2,4-Trichlorobenzene	39-98	38-107
BN	Acenaphthene	46-118	31-137
BN	2,4-Dinitrotoluene	24-96	28-89
BN	Pyrene	26-127	35-142
BN	N-Nitroso-Di-n-Propylamine	41-116	41-126
BN	1,4-Dichlorobenzene	36-97	28-104
Acid	Pentachlorophenol	09-103	17-109
Acid	Phenol	12-110	26-90
Acid	2-Chlorophenol	27-123	25-102
Acid	4-Chloro-3-Methylphenol	23-97	26-103
Acid	4-Nitrophenol	10-80	11-114
PCDX	Polychlorinated Dibenzo-p-Dioxins/Furans	60-150	60-150
Extractable Organics by GC			
Pest	Lindane	56-123	46-127
Pest	Heptachlor	40-131	35-130
Pest	Aldrin	40-120	34-132
Pest	Dieldrin	52-126	31-134
Pest	Endrin	56-121	42-139
Pest	4,4'-DDT	38-127	23-134
Inorganics			
	Metals	75-125	75-125
	Wet Chemistries	75-125	75-125

These are USEPA CLP advisory limits, with the exception of PCDX and the wet chemistries.

Matrix spike recoveries may be highly affected by the nature of the sample spiked. Mild to severe matrix interferences are frequently encountered with environmental samples; therefore, recoveries outside of the limits may simply demonstrate the effect of the matrix on analyte recovery given the limitations of the methods performed.

Limits are not solely used to determine if a sample should be reanalyzed; matrix spike recovery contributes to the overall quality control assessment of analytical data and any subsequent corrective actions taken by the laboratory as a result of its evaluation.

Table 5.2 Core Duplicate Relative Percent Difference (RPD) Limits

Fraction	Parameter	Water	Soil
Volatile Organics by GC/MS			
VOA	1,1-Dichloroethene	14	22
VOA	Trichloroethene	14	24
VOA	Chlorobenzene	13	21
VOA	Toluene	13	21
VOA	Benzene	11	21
Extractable Organics by GC/MS			
BN	1,2,4-Trichlorobenzene	28	23
BN	Acenaphthene	31	19
BN	2,4-Dinitrotoluene	38	47
BN	Pyrene	31	36
BN	N-Nitroso-Di-n-Propylamine	38	38
BN	1,4-Dichlorobenzene	28	27
Acid	Pentachlorophenol	50	47
Acid	Phenol	42	35
Acid	2-Chlorophenol	40	50
Acid	4-Chloro-3-Methylphenol	42	33
Acid	4-Nitrophenol	50	50
PCDX	Polychlorinated Dibenzo-p-Dioxins/Furans	50	50
Extractable Organics by GC			
Pest	Lindane	15	50
Pest	Heptachlor	20	31
Pest	Aldrin	22	43
Pest	Dieldrin	18	38
Pest	Endrin	21	45
Pest	4,4'-DDT	27	50
Inorganics			
	Metals (a)	20	20
	Cyanides (a)	20	20
	Wet Chemistries (b)	25	25

These are USEPA CLP RPD advisory limits, with the exception of PCDX and the wet chemistries.

The RPD of duplicated environmental samples may be highly affected by the nature of the sample matrix. Mild to severe heterogeneity is frequently encountered within a sample; this may result in variable matrix interferences or concentrations of analytes inherently present. Therefore, elevated RPDs may simply demonstrate the effect of the matrix on precision given the limitations of the methods performed.

Limits are not solely used to determine if a sample should be reanalyzed; the RPD contributes to the overall quality control assessment of analytical data and any subsequent corrective actions taken by the laboratory as a result of its evaluation.

Footnotes:

(a) +/- CRDL WHEN <5X CRDL; +/-20% WHEN >5X CRDL

(b) +/- 50% WHEN <5X MDL; +/- 25% WHEN >5X MDL

Table 5.3 Core Surrogate/System Monitoring Compound (SMC) Recovery Limits

Fraction	Surrogate/SMC Compound	Water	Low/Med Soil
SW846, 600s, 2/88 CLP			
Volatile (GC/MS)	Toluene-d_8	88-110	81-117
	4-Bromofluorobenzene	86-115	74-121
	1,2-Dichloroethane-d_4	76-114	70-121
Volatile (GC-VHC)	1,4-Dichlorobutane	80-120	80-120
Volatile (GC-VAr)	a,a,a-Trifluorotoluene	80-120	80-120
Acid (GC/MS)	Phenol-d_5	10-94	24-113
	2-Fluorophenol	21-100	25-121
	2,4,6-Tribromophenol	10-123	19-122
Base/Neutral (GC/MS)	Nitrobenzene-d_5	35-114	23-120
	2-Fluorobiphenyl	43-116	30-115
	Terphenyl-d_{14}	33-141	18-137
Pest/PCB (GC-ECD)	Dibutylchlorendate	24-154 (a)	20-150 (a)
	Tetrachloro-m-xylene	46-185	34-160
Pesticide (GC-FPD)	Ethyl-p-nitrophenyl-benzenethiophosphonate	24-154	20-150
Herbicide (GC-ECD)	Dicamba	03-143	03-143
PCDX (GC/MS)	13C-isomers (b)	10-120	10-120
3/90 CLP, OLM01			
Volatile (GC/MS)	Toluene-d_8	88-110	84-138
	4-Bromofluorobenzene	86-115	59-113
	1,2-Dichloroethane-d_4	76-114	70-121
Acid (GC/MS)	Phenol-d_5	10-110	24-113
	2-Fluorophenol	21-110	25-121
	2,4,6-Tribromophenol	10-123	19-122
	2-Chlorophenol-d_4	33-110 (a)	20-130 (a)
Base/Neutral (GC/MS)	Nitrobenzene-d_5	35-114	23-120
	2-Fluorobiphenyl	43-116	30-115
	Terphenyl-d_{14}	33-141	18-137
	1,2-Dichlorobenzene-d_4	16-110 (a)	20-130 (a)
Pesticides (GC)	Decachlorobiphenyl	60-150 (a)	60-150 (a)
	Tetrachloro-m-xylene	60-150 (a)	60-150 (a)

Footnotes:
(a) Advisory limits; not solely used to determine if a sample should be reanalyzed.
(b) Internal Standards (IS) are added at preparation for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDX). The recovery standard is added at analysis to quantitate IS concentration and determine % recoveries. The IS compounds are included as functional surrogate compounds for the method performed.

Table 6.1 Containers, Holding Times and Preservatives

Parameter	Container (a)	Holding Time (b)	Preservative (c)
Wet Chemistry, Standard Analyses			
Total Organic Carbon (TOC)	1 x 125 ml, g	28 days	H_2SO_4, pH < 2; Cool, 4° C
Total Organic Halides (TOX; dupl/quadruplicate)	1 x 500 ml; or 2 x 500 ml, g (d)	28 days	H_2SO_4, pH < 2; $NaSO_3$
Chemical Oxygen Demand (COD)	1 x 125 ml, g	28 days	H_2SO_4, pH < 2; Cool, 4° C
Total Petroleum Hydrocarbons	1 x 1 L, g	28 days	H_2SO_4, pH < 2; Cool, 4° C
Cyanide, Total (in-line/manual distillation)	1 x 125 ml; or 1 x 1 L, g	14 days	NaOH, pH > 12; Cool, 4° C
Phenolics, Total (in-line/manual distillation)	1 x 125 ml; or 1 x 500 ml, g	28 days	H_2SO_4, pH < 2; Cool, 4° C
Sulfate	1 x 125 ml, g	28 days	Cool, 4° C
Chloride	1 x 125 ml, g	28 days	Cool, 4° C
Nitrate as N	1 x 125 ml, g	28 days	H_2SO_4, pH < 2; Cool, 4° C
Nitrite as N	1 x 125 ml, g	28 days	H_2SO_4, pH < 2; Cool, 4° C
Fluoride	1 x 125 ml, g	28 days	Cool, 4° C
Specific Conductance	1 x 500 ml, g	28 days	Cool, 4° C
Total Solids	1 x 500 ml, g	7 days	Cool, 4° C
Total Dissolved Solids	1 x 500 ml, g	7 days	Cool, 4° C
Total Suspended Solids	1 x 500 ml, g	7 days	Cool, 4° C
Sulfide	2 x 125 ml, g (d)	7 days	Zn acetate & NaOH, pH > 9; Cool, 4° C
Inorganics, Standard Analyses			
Metals, except Mercury	1 x 1 L, p or g	6 months	HNO_3, pH < 2; Cool, 4° C
Mercury	1 x 1 L, g	28 days (e)	HNO_3, pH < 2; Cool, 4° C
Organics, Standard Analyses			
Volatiles, purge & trap (GC/MS)	3 x 40 ml, g (d)	14 days (f)	HCl, pH < 2; Cool, 4° C
Volatiles, heated purge & trap (GC/MS)	3 x 40 ml, g (d)	14 days (f)	HCl, pH < 2; Cool, 4° C

Table 6.1 Continued

Parameter	Container (a)	Holding Time (b)	Preservative (c)
Purgeable Aromatics (GC)	3 x 40 ml, g (d)	14 days (f)	HCl, pH < 2; Cool, 4° C
Purgeable Halocarbons (GC)	3 x 40 ml, g (d)	14 days	Cool, 4° C (m)
Semivolatiles, Acid/base/neutral (GC/MS)	2 x 1 L, g	7/14 days (prep); 40 days (analysis)(g)	Cool, 4° C
Pesticides and/or Aroclors (GC, GC/MS)	2 x 1 L, g	7/14 days (prep); 40 days (analysis)(g)	Cool, 4° C
Herbicides (GC)	2 x 1 L, g	7/14 days (prep); 40 days (analysis)(g)	Cool, 4° C
Polychlorinated Dibenzo-p-Dioxins/Furans (GC/MS)	2 x 1 L, g (water)	7 days (prep); 40 days (analysis)(g)	Cool, 4° C
	1 x 500 ml, g (soil)	30 days (prep); 45 days (analysis)	
Polynuclear Aromatic Hydrocarbons (HPLC)	2 x 1 L, g	7/14 days (prep); 40 days (analysis)(g)	Cool, 4° C
Toxicity Characteristic Leaching Procedure (k) Preparation of the TCLP Extract			
Volatiles	1 x 125 ml, g (d)	14 days	Cool, 4° C (h)
Semi-volatiles	1 x 1L, g	14 days	Cool, 4° C (h)
Metals, except Mercury	1 x 1L, p or g	180 days	Cool, 4° C (h)
Mercury	1 x 1L, p or g	28 days	Cool, 4° C (h)
Toxicity Characteristic Constituents Analysis of the TCLP Extract			
Volatiles, purge & trap	3 x 40 ml, g (d)	14 days (i)	HCl, pH < 2; Cool, 4° C
Semi-volatiles, Acid/base/neutral, pesticides	2 x 1 L, g (d)	7 days (prep)(i) 40 days (analysis)(g)	Cool, 4° C
Semi-volatiles, Herbicides	2 x 1 L, g (d)	7 days (prep)(i) 40 days (analysis)(g)	Cool, 4° C
Metals, except Mercury	1 x 1 L, p	180 days (i)(j)	HNO_3, pH < 2 (j)
Mercury	1 x 1 L, g	28 days (i)(j)	HNO_3, pH < 2 (j)
U.S. EPA CLP Parameters (l)			
Volatile Organics	3 x 40 ml; g (d)	10 days	HCl, pH < 2; Cool, 4° C
Semivolatile Organics (BNA)	2 x 1 L; g	5/10 days (prep); 40 days (analysis)(g)	Cool, 4° C

Table 6.1 Continued

Parameter	Container (a)	Holding Time (b)	Preservative (c)
Semivolatile Organics (Pest/PCB)	2 x 1 L; g	5/10 days (prep); 40 days (analysis)(g)	Cool, 4° C
Metals (except Mercury)	1 x 1 L; p	6 months	HNO_3, pH < 2; Cool, 4° C
Mercury	1 x 1 L; p	26 days	HNO_3, pH < 2 Cool, 4° C
Cyanide, Total	1 x 1 L, g	12 days	NaOH, pH > 12; Cool, 4° C

Notes: g = glass; p = plastic

Sulfide is a subcontract parameter.

Source: 40 CFR Part 136 Table II; SW-846 3rd Edition; U.S. EPA CLP Statements of Work.

Footnotes:

(a) Minimum volume requirements for aqueous samples are listed for extractable organic parameters by GC and GC/MS methods. An additional two (2) liters are required for matrix spike and matrix spike duplicate preparation for each analytical method when the sample is utilized for QC purposes.

Lesser sample amounts may be required for soil/sediment samples.

(b) Hold time from date of sampling unless otherwise noted; Aqueous/Non-aqueous where applicable.

(c) Chemical preservation is not applicable to non-aqueous matrices. Premeasured amounts of preservatives are supplied in small ampules attached to the proper bottles for water matrices.

(d) Filled with minimal headspace to prevent analyte loss.

(e) For SW846 Update I, 13 days if container is plastic.

(f) If pH > 2, hold time is shortened to 7 days.

(g) Hold time from date of preparative extraction.

(h) No chemical preservatives should be added to samples prior to TCLP extraction; samples may be cooled as indicated unless refrigeration results in irreversible physical changes to the sample. The laboratory should be informed if precipitation occurs so that the entire sample, including the precipitate, may be extracted.

(i) Hold time from completion date of TCLP extract preparation.

(j) If precipitation is observed upon addition of nitric acid to a small aliquot of the TCLP extract, the remaining portion will not be acidified and the extract will be analyzed as soon as possible.

(k) Minimum estimated volume requirements for the intact sample are listed for the leaching procedure. Additional sample may be required depending on the physical nature of the sample and/or matrix spike preparation. Should this be the case, the laboratory will contact the client immediately for resolution. The laboratory will send extra bottles for the initial sampling event if there is reason to believe or concern that the volumes stated will not satisfy the mass (weight) requirements of the method.

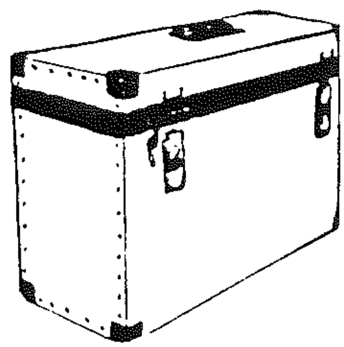
(l) Hold time from verified time of sample receipt (VTSR) at the laboratory.

(m) May be acidified to pH < 2 with HCl; laboratory can provide nonacidified bottles upon client request.

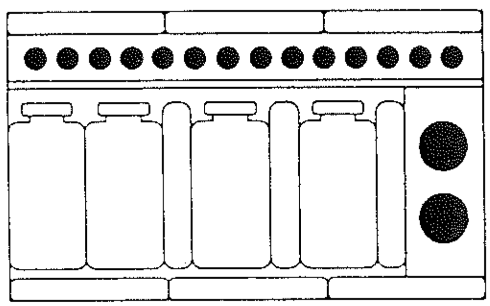
Figure 6.1 Sample Shuttle™

The Sample Shuttle™ is a uniquely engineered and patented shipping container that has been designed to meet and exceed USEPA and State protocols for shipping, chemical and thermal preservation of analytical samples. The container can be locked and sealed to ensure sample integrity during both transport and sampling.

Diagram of Shuttle & Example Bottle Configuration



Exterior



Interior - Cross Section
Example Configuration

Features Include:

A convenient suitcase shape for ease of transportation to and from sampling locations;

A rugged waterproof outer container that withstands varying field conditions;

Polyurethane foam insulation for dependable thermal performance;

Chain of Custody locks and numbered seals preserve sample integrity;

Customized coolant to sustain required EPA temperature controls;

Chain of Custody and Field Parameter forms to document sampling event;

Polyethylene modular sleeve designed to prevent bottle breakage during shipment;

Pre-labeled, pre-configured bottles specific for each sampling event;

Pre-measured preservatives are attached to bottles with color coded instructions to ensure proper protocols are followed; and

Return shipping labels and custody seals to provide rapid correct return of samples to the lab.

Figure 6.1 continued

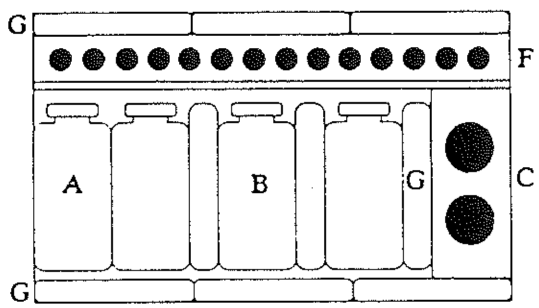
Sample Shuttle Instructions
Please Read Carefully Before Sampling

1. Freeze the ice packs at least 24 hours before sampling if the ice packs are requested from the laboratory in their unfrozen state.

2. Break the black seal on the shuttle hasp. Open the shuttle and remove the plastic bag which contains: Chain-of-Custody form, Field Information form, return shipping label, clear blank shuttle seals (for temporary custody), one black numbered shuttle seal (for resealing the shuttle after sampling).

3. Examine the Chain-of-Custody and Field Information forms carefully. These must be filled out and returned for accurate processing of the samples. Note any relevant information on the forms. Please call the Core Project Manager with any questions.

4. Unpack the bottles and frozen/unfrozen ice packs. Note the order of packing. The shuttle should be repacked exactly as received. This prevents bottle breakage and/or sample freezing from occurring.



A) 1 L Plastic Bottle
B) 1 L Amber Glass Bottle
C) 125 ml Amber Glass Bottle
D) 500 ml Plastic Bottle
E) 500 ml Amber Glass Bottle
F) 40 ml Glass Vial
G) Ice Packs

Example Configuration

5. Each bottle is labeled with a Core sample number (ie., GFK046) and the analysis to be performed (ie., TOC, VOA). Match the type of analysis and quantity of bottles against the Chain-of-Custody form. Be sure that all bottles used for a single sample point have the same Core number. Chemical preservative solutions are in ampules attached to the bottles that will require chemical preservation.

6. After sampling and repacking the shuttle, place all completed forms into the plastic bag and place the bag into the shuttle; close the lid.

7. Apply the return shipping label on the outside of the shuttle.

8. Insert the black custody seal through one of the outside shuttle latches and lock it.

9. When Emergency or Express analysis has been requested or is found to be needed, please call the Core Project Manager and give the following shipping information: a) Carrier, b) Airbill number, c) Arrival Date, and d) Number of shuttles.

10. When anticipated sampling or send dates change, please call the Core Project Manager so that the laboratory can most accurately schedule for the samples.

Sampling Notes

For TOX and VOA samples, fill the bottle leaving no headspace (no air bubbles).

Add the ampulated acid preservative solutions to the bottles after sampling.

Indicate on the Chain-of-Custody form whether the sample has been filtered.

CORE LAB

CORE LABORATORIES, INC.

NO. 62002

CHAIN OF CUSTODY R ORD

CUSTOMER INFORMATION	PROJECT INFORMATION
COMPANY	PROJECT NAME/NUMBER
SEND REPORT TO	**BILLING INFORMATION**
ADDRESS	BILL TO
	ADDRESS
PHONE:	PHONE:
FAX	FAX: PO NO

NUMBER OF CONTAINERS

ANALYSIS / METHOD REQUEST

LAB JOB NO.

SAMPLE NO.	SAMPLE DESCRIPTION	SAMPLE DATE	SAMPLE TIME	SAMPLE MATRIX	CONTAINER	PRESERV.										REMARKS / PRECAUTIONS

SAMPLER	SHIPMENT METHOD	AIRBILL NO :

REQUIRED TURNAROUND * [ ] SAME DAY [ ] 24 HOURS [ ] 48 HOURS 72 HOURS 5 DAYS 10 DAYS ROUTINE OTHER ________

1. RELINQUISHED BY: SIGNATURE	DATE	2. RELINQUISHED BY: SIGNATURE	DATE	3. RELINQUISHED BY: SIGNATURE	DATE
PRINTED NAME/COMPANY	TIME	PRINTED NAME/COMPANY	TIME	PRINTED NAME/COMPANY	TIME
1. RECEIVED BY: SIGNATURE	DATE	2. RECEIVED BY: SIGNATURE	DATE	3. RECEIVED BY: SIGNATURE	DATE
PRINTED NAME/COMPANY.	TIME	PRINTED NAME/COMPANY	TIME	PRINTED NAME/COMPANY	TIME

* RUSH TURNAROUND MAY REQUIRE SURCHARGE

☐ **Anaheim, CA**
1250 E. Gene Autry Way
Anaheim,CA 92805
(714) 937-1094 Fax (714) 937-1170

☐ **Aurora, CO**
10703 E. Bethany Drive
Aurora, CO 80014
(303) 751-1780 Fax (303) 751-1784

☐ **Casper, WY**
420 W. First Street
Casper, WY 82601
(307) 235-5741 Fax (307) 266-1676

☐ **Corpus Christi, TX**
1733 N. Padre Island Drive
Corpus Christi, TX 78408
(512) 289-2673 Fax (512) 289-2471

☐ **Edison, NJ**
284 Raritan Center Parkway
Edison, NJ 08837
(908) 225-6700 Fax (908) 225-6777

☐ **Houston, TX (Env)**
8310 Rothway Drive
Houston, TX 77040
(713) 690-4444 Fax (713) 690-5646

☐ **Houston, TX (Pet)**
8210 Mosley Road
Houston, TX 77075
(713) 943-9776 Fax (713) 943-3846

☐ **Indianapolis, IN**
7726 Moller Road
Indianapolis,IN 46268
(317) 875-5894 Fax (317) 872-6189

☐ **Lake Charles, LA**
3645 Beglis Parkway
Sulphur, LA 70663
(318) 583-4926 Fax (318) 583-4929

☐ **Long Beach, CA**
3700 Cherry Avenue
Long Beach, CA 90807
(310) 595-8401 Fax (310) 427-5174

☐ **Tampa, FL**
5460 Beaumont Center Blvd.
Tampa, FL 33634
(813)884-8268 Fax (813) 885-4938

☐ **Valparaiso, IN**
2400 Cumberland Drive
Valparaiso, IN 46383
(219) 464-2389 Fax (219) 462-2953

ORIGINAL

PACE ENVIRONMENTAL LABORATORIES

Figure 7.1

CHAIN OF CUSTODY FORM (CC1)

Seal No. ____________ PACE Job # ____________

Date Sealed ____________ By: ____________

Company: ____________ Attn.: ____________

Facility/Site: ____________ Phone: ____________

Address: ____________

SAMPLE IDENTIFICATION

Facility: Facility/Site Code; (Optional Sample Point Descriptions)

Sample Point: Source Code (from below) – Your Sample Point ID (left justify); Start Date (YY/MM/DD); Start Time (2400 hr. clock); Elapsed Hours (composite)

Source Codes:

Well ..(W) Outfall.......(O) Bottom Sediment ....(B) Surface Impoundment....(I) Leachate Collection Sys.....(C) Other ....(X)

Soil ....(S) River/Stream...(R) Generation Point ... (G) Treatment Facility ......(T) Lake/Ocean .... (L) Specify ____________

SHUTTLE CONTENTS

BOTTLE				ANALYSIS	SAMPLER		LAB
No	Type	Size	Preserv.		Filt. (Y/N)	Observations	Observations

CHAIN OF CUSTODY CHRONICLE

1. Shuttle Opened By: (print) ____________ Date: ____________ Time: ____________
Signature: ____________ Seal #: ____________ Intact: ____________

2. I have received these materials in good condition from the above person.
Name: ____________ Signature: ____________
Date: ____________ Time: ____________ Remarks: ____________

3. I have received these materials in good condition from the above person.
Name: ____________ Signature: ____________
Date: ____________ Time: ____________ Remarks: ____________

4. Shuttle Sealed By: (print) ____________ Date: ____________ Time: ____________
Signature: ____________ Seal #: ____________ Intact: ____________

LAB USE ONLY Opened By: ____________ Date: ____________ Time: ____________

SHUTTLE # ____________ TEMP. °C ____________ SEAL # ____________ COND. ____________

pace. INCORPORATED
ENVIRONMENTAL LABORATORIES

27‘428

CHAIN-OF-CUSTODY RECORD
Analytical Request

Client	Report To:	Pace Client No.
Address	Bill To:	Pace Project Manager
	P.O. # / Billing Reference	Pace Project No.
Phone	Project Name / No.	*Requested Due Date:

Sampled By (PRINT):

Sampler Signature | Date Sampled

ITEM NO.	SAMPLE DESCRIPTION	TIME	MATRIX	PACE NO.	NO. OF CONTAINERS	PRESERVATIVES: UNPRESERVED	H_2SO_4	HNO_3	VOA			ANALYSES REQUEST	REMARKS
1													
2													
3													
4													
5													
6													
7													
8													

For Interim Use - Core Laboratories, Inc., Edison, New Jersey - January, 1996

COOLER NOS.	BAILERS	SHIPMENT METHOD OUT/DATE	SHIPMENT METHOD RETURNED/DATE

ITEM NUMBER	RELINQUISHED BY / AFFILIATION	ACCEPTED BY / AFFILIATION	DATE	TIME

Additional Comments

Figure 7.2

SEE REVERSE SIDE FOR INSTRUCTIONS

ORIGINAL

PACE INCORPORATED
ENVIRONMENTAL LABORATORIES

Figure 7.3

FIELD PARAMETER FORM (CC2)

Form 0002
Sample Management
10/94

PACE JOB # ______________________

Sample Point [ ] Source Code [| | | | | | | | | |] Sample Point I.D.

FIELD PROCEDURES

[| | | | |]	[| | |]	[| |]	[| | | |]	[| | | |]
PURGE DATE (YY MM DD)	START PURGE (2400 Hr Clock)	ELAPSED HRS	WATER VOL. IN CASING (Gallons)	VOLUME PURGED (Gallons)

SAMPLING METHOD: ______________________

Sampler Type [ ] A-Submersible Pump, B-ISCO, C-Bladder Pump; D-Dipper/Bottle, E-Bailer, F-Scoop/Shovel; X-Other ______________ (SPECIFY OTHER)

Sampler Material [ ] A-Teflon, B-Metal; C-PVC, D-Plastic; X-Other ______________ (SPECIFY OTHER)

Tubing Material [ ] A-Teflon, B-Tygon; C-Polyethylene, D-Silicon; X-Other ______________ (SPECIFY OTHER)

Sample Composited [Y/N] ______________ Procedure/Proportions

FIELD MEASUREMENTS

Well Elevation (ft/msl) [| | | | . |]

Depth to Ground water (ft) [| | | | . |]

Groundwater Elevation (ft msl) [| | | | . |]

Well Depth (ft) [| | | . |]

Sample Depth (non-well) (ft) [| | | . |]

	ph			spec. cond.		(other parameter)	value	units
	[| | |]	(STD)	1st	[| | | |]	um/cm at 25° C	[ ]	[| | | |]	[ ]
2nd	[| | |]	(STD)	2nd	[| | | |]	um/cm at 25°C	[ ]	[| | | |]	[ ]
3rd	[| | |]	(STD)	3rd	[| | | |]	um/cm at 25°C	[ ]	[| | | |]	[ ]
4th	[| | |]	(STD)	4th	[| | | |]	um/cm at 25°C	[ ]	[| | | |]	[ ]

[| | |] (°C) Sample Temp

[| | | |] NTU Turbidity

FIELD COMMENTS

Sample Appearance: ______________________

Weather Conditions: ______________________

Other: ______________________

For Interim Use - Core Laboratories, Inc., Edison, New Jersey - January, 1996

____

____

FILTERING: Use Chain of Custody (CC1) to indicate which bottles were filtered

Sampler: ______________ (Print) Employer: ______________

I certify that sampling procedures were in accordance with applicable EPA state and corporate protocols.

____

(Date) (Signature)

ORIGINAL

Figure 7.4

CORE Laboratories

CHAIN OF CUSTODY

COMPANY: ______________________________

ADDRESS: ______________________________

____

ATTN: ______________________________

SAMPLE DESCRIPTION:

CUSTOMER ID	DESCRIPTION	SAMPLING DATE	LAB ID

Sample(s) relinquished by: ______________________________ Date: ________ Time: ______

Sample(s) received by: ______________________________ Date: ________ Time: ______

ıttle #: ____________________ Seal Number: ____________________ Temp: __________

Figure 7.5

CORE LABORATORIES

SAMPLE RECEIPT CHECKLIST				
LOGLINK:				CLIENT:
DATE REC'D.:				DATE SAMPLED:
PROJECT:				SDG:
SAMPLE MANAGER:	N/A	YES	NO	COMMENTS/RESOLUTION
AIRBILL/# CONTAINERS CORRECT				
CORE JOB NUMBERS PRESENT				
CUSTODY SEALS INTACT				
SAMPLE TEMP. 2-6 DEG. C.				
SAMPLED WITHIN 24 HRS. OF RECEIPT				
SAMPLES PRESERVED PROPERLY				
NO HEAD SPACE (VOA, TOX)				
SAMPLE BOTTLES INTACT				
PROJECT MANAGER:	N/A	YES	NO	COMMENTS/RESOLUTION
CHAIN OF CUSTODY FILLED OUT PROPERLY				
CHAIN OF CUSTODY MATCHES SAMPLES				
SAMPLES MATCH ORDER				
PROPER BOTTLES AND VOLUMES				
ADDITIONAL COMMENTS BY SAMPLER				
TPM REVIEW:				DATE:
CLIENT CONTACT:				DATE:
OTHER NOTES/COMMENTS:				

Figure 7.6

```
                    CORE/New Jersey Laboratory
              LOGIN CHAIN OF CUSTODY REPORT (ln01)
                      Jan 30 1996, 02:35 pm

                      Login Number: LBMC6
           Receive Date Range: 30-JAN-96 thru 30-JAN-96
                 Account: A-150  PACE/NJ QA
             Project: HCLMONITOR  HCL MONITORING

Laboratory              Client                   Collect   Receive        Due
SampleNumber        SDG SampleNumber             Date      Date       PR Date
-------------------------------------------------------------------------------
BMC6-17            5298 HA013096                 30-JAN-96 30-JAN-96     27-FEB-96
SPECVOA: RESULTS MUST BE SUBMITTED TO QA ASAP AFTER ANALYSIS.  TIC/QUANT,
SPECTRA, INTERNAL C-OF-C AND LAB CHRONICLE FOR SAMPLE AND BATCH BLANK MUST
BE SUBMITTED.  SPECRP: DO NOT GENERATE REPORT.
Aqueous     S 624/TCL/VOA          ETED Hold:13-FEB 408008
No Matrix   S CASE REPORT          ETED             408008
No Matrix   S SPECRP               ETED Hold:27-FEB 408008
Aqueous     S SPECVOA              ETED Hold:13-FEB 408008
Aqueous     S TIC/VOA+15           ETED Hold:13-FEB 408008
```


Date:

Figure 7.7

Daily Receipt Log

pace INCORPORATED ENVIRONMENTAL LABORATORIES

DATE ____________

TIME ____________

COURIER ____________

CLIENT ____________

RECEIVED BY: ____________

RELINQUISHED BY: ____________

\# OF COOLERS ____________

\# OF SHUTTLES ____________

\# OF ENVELOPES ____________

\# OF OTHER ____________

TOTAL ____________

DELIVERED TO: ____________

Daily Receipt Log

pace INCORPORATED ENVIRONMENTAL LABORATORIES

DATE ____________

TIME ____________

COURIER ____________

CLIENT ____________

RECEIVED BY: ____________

RELINQUISHED BY: ____________

\# OF COOLERS ____________

\# OF SHUTTLES ____________

\# OF ENVELOPES ____________

\# OF OTHER ____________

TOTAL ____________

DELIVERED TO: ____________

Daily Receipt Log

pace INCORPORATED ENVIRONMENTAL LABORATORIES

DATE ____________

TIME ____________

COURIER ____________

CLIENT ____________

RECEIVED BY: ____________

RELINQUISHED BY: ____________

\# OF COOLERS ____________

\# OF SHUTTLES ____________

\# OF ENVELOPES ____________

\# OF OTHER ____________

TOTAL ____________

DELIVERED TO: ____________

Daily Receipt Log

pace INCORPORATED ENVIRONMENTAL LABORATORIES

DATE ____________

TIME ____________

COURIER ____________

RECEIVED BY: ____________

RELINQUISHED BY: ____________

\# OF COOLERS ____________

\# OF SHUTTLES ____________

\# OF ENVELOPES ____________

\# OF OTHER ____________

TOTAL ____________

DELIVERED TO: ____________

Figure 7.8

CORE Laboratories

SUBCONTRACT ANALYSES AND SAMPLE CHAIN-OF-CUSTODY

Subcontract Laboratory: ______________________

Loglink(s): ______________________

Matrix: ____________ Sample Date(s): ____________

Deliverables: ______________________

CORE Laboratories Sample ID #'s: ______________________

Faxed data due by: ____________ Hardcopy report due by: ____________

If deadline cannot be met, contact CORE Laboratories Subcontract Department at 908/225-6700.
Send report & invoice to CORE Laboratories, 284 Raritan Ctr Pkwy, Edison, NJ 08837 Attn: Subcontract Dept

The following analyses are requested (list bottle type):

______	ACIDITY	______	FLUORIDE	______	SOLIDS/TV
______	ALKA	______	FORM/UV	______	SO4
______	NH3	______	HARD	______	SULFIDE
______	NH3/D	______	NO3	______	SO3
______	BICARB	______	NO2	______	SURFAC
______	BOD	______	N2/ORG	______	TOX
______	BROM	______	N2/TK	______	TOX2
______	BTU	______	ODOR	______	TOX4
______	CARB	______	O+G/GRAV	______	TOC2
______	CA/CAC03	______	O+G/IR	______	TOC4
______	CHLOR	______	PHENOLS	______	TURB
______	CL2/T	______	PHENOLS/DL	______	AP9/SULFIDE
______	CL2/D	______	PO4/T	______	M601
______	CL2/R	______	PO4/ORG	______	M602
______	COD	______	PO4/ORT	______	M603
______	COLI/F	______	PHOS	______	M503.1
______	COLI/T	______	CY/REACT	______	M524.2
______	COLOR/S	______	SULFIDE/REACT	______	BTXE
______	COLOR/A	______	SOLIDS/T	______	MTBE
______	CR(+6)	______	SOLIDS/TD	______	PP/PEST
______	CY (CHLOR)	______	SOLIDS/SETL	______	PP/PCB
______	CY/T	______	SOLIDS/TS	______	PP/PCB

Other: ______________________

____

CHAIN-OF-CUSTODY (COMPLETE APPROPRIATE SECTION)

OPTION A: COURIER PICKUP AT CORE Laboratories

Sample(s) relinquished by CORE Laboratories: ____________ Time: ________ Date: ______

Sample(s) received by : ____________ Time: ________ Date: ______

OPTION B: SENDING SAMPLE FROM CORE Laboratories

Shuttle sealed at CORE Laboratories by: ____________ Seal #: ________ Time: ________ Date:

Shuttle opened by: ____________ Seal #: ________ Time: ________ Date: ________

Seal intact? YES _____ NO _____ Shuttle contents in good condition? YES _____ NO _____

COMMENTS: ______________________

CORE Laboratories

REQUEST FOR SUBCONTRACT ANALYSES AND SAMPLE CHAIN-OF-CUSTODY

Subcontract Laboratory: ______________________________

Loglink(s): ____________________ Project Name: ______________

Contact: ______________ Phone: ______________

CORE Laboratories Sample ID #'s: ______________________________

____

Matrix: ____________ Received at Core Laboratories: __________ Sample Date: ________

Due Date: Faxed: __________ Hardcopy: ________

Deliverables Required (Check if needed):

Results: ________ QC Data: ________ Raw Data: ________ Internal Chain of Custody: ________

Prep & Analysis Dates: ____________ Other: ______________

If deadline cannot be met, contact CORE Laboratories Subcontract Department at 908/225-6700.
Send report & invoice to CORE Laboratories, 284 Raritan Ctr Pkwy, Edison, NJ 08837 Attn: Subcontract Dept

The following analyses are requested:

PARAMETERS	METHOD	# BOTTLES/TYPE	DL'S REQUIRED

ADDITIONAL REQUIREMENTS: ______________________________

CHAIN-OF-CUSTODY (COMPLETE APPROPRIATE SECTION)

OPTION A: COURIER PICKUP AT CORE Laboratories

Sample(s) relinquished by CORE Laboratories: ______________ Time: ________ Date: ______

Sample(s) received by : ______________ Time: ________ Date: ______

Seal intact? YES ____ NO ____ Shuttle contents in good condition? YES ____ NO ____

OPTION B: SENDING SAMPLE FROM CORE Laboratories

Shuttle sealed at CORE Laboratories by: ______________ Seal #: ________ Time: ______ Date:

Shuttle opened by: ______________ Seal #: ________ Time: ______ Date: ______

Seal intact? YES ____ NO ____ Shuttle contents in good condition? YES ____ NO ____

COMMENTS: ______________________________

CORELAB

LABORATORY ANALYSIS REQUEST LOG

SHIPPING LOCATION	RECEIVING LOCATIONS & FAX NUMBER (checkmark)			
Shipping Location Contact	714-937-1170 Anaheim, CA		713-943-3846 Houston, TX (Pet)	
Receiving Location Contact	303-751-1784 Aurora, CO		317-872-6189 Indianapolis, IN	
Date Initiated	307-266-1676 Casper, WY		318-583-4929 Lake Charles, LA	
Shipment Method	512-289-2471 Corpus Christi, TX		310-427-5174 Long Beach, CA	
Shipment Date	908-225-6777 Edison, NJ		813-885-4938 Tampa, FL	
	713-690-5646 Houston, TX (Env)		219-462-2953 Valparaiso, IN	
	Other (specify)			

PROJECT NO./ SAMPLE ID	MATRIX	ANALYSIS REQUESTED	METHOD	REPORTING LIMIT	PRICE	DUE DATE

SPECIAL REQUIREMENTS	Y	N	Specify Requirements - If necessary, attach additional documentation
Rush turnaround requirements?			
Special report delivery (FAX, FedEx, etc.)?			
Specific detection limits or reporting units?			
Specific QC samples or deliverables?			
Copies of raw laboratory data?			
Report or invoice to client or other parties?			

SHIPPING LOCATION'S COMMENTS:	RECEIVING LOCATION'S COMMENTS:

SHIPPING LOCATION'S APPROVAL

Approved By ______________________

Date ______________________

RECEIVING LOCATION'S APPROVAL

Approved By ______________________

Date ______________________

LARL.LOG
1/96

NOTE: All sections must be completed to ensure that client requirements are met. QA reports must be included with all sample results.

Figure 7.10

CORE Laboratories

INTERNAL CHAIN-OF-CUSTODY

Client: ______________________ Analytical Parameter/Fraction: ______________________

Sample No.	Sample No.	Sample No.	Sample No.	Sample No.	Sample No.

DATE/TIME		RELINQUISHED BY	RECEIVED BY	PURPOSE OF CHANGE OF CUSTODY
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			
	PRINTED NAME: SIGNATURE:			

Figure 7.11

CORE/New Jersey Laboratory — LAB CHRONICLE: Sample Preparation (wk02s) — Jan 22 1996

WORK GROUP: OW43509 — SCHEDULER: — CREATED : 19-JAN-96 — DUE:

Sample	SDG Locatn	Ver Sur	Sample Amt. ml (gm)	Moisture %	Dry Wt. gm	EXT VOL (ml)		HOLD	VB DUE	HC DUE	REPEAT Orig QS No.	M	ANALYSIS
BMF2-00	5256 407967		20.0			100		02/15	02/02			2	418.1/TPH

		Ver Sur	Sample Amt.	Moisture	Dry Wt.	EXT VOL		Verify	Spike
QS 43509						100			
QS 43509	s1					100		MS/fsh	1/22/96
BMF200	ms1		20.0			100		MS/fsh	1/22/96
BMF200	msd1		20.0			100		MS/fsh	1/22/96
QS 43509 E.P.A						100			
QS	s2								
	ms2								
	msd2								

Comments:

PROCEDURE:

	C1 SIGNATURE	C1 DATE	C2 SIGNATURE	C2 DATE
__ CONTINUOUS				
__ SEP. FUNNEL				
SONICATION				
X SOXHLET	MS/fsh	1/22/96		
__ DILUTION				
__ DERIVATION				
_ A/B PART.				
FLORISIL CART.				
__ ALUMINA				
__ SULF/COPPER				
__ GPC				
__ CONC.				

SPIKE	VOL ml	CONC. ug/ml	mg/ml	LOT NUMBER
BLANK Spike	1.0	2.0		379
E.P.A	1.0	20		575
MS	2.0	10		535

SURROGATES

SOLVENT	LOT NUMBER

REAGENT	LOT NUMBER
Sodium Sulfate	
Florisil	

Matrix: __ Water X Soil __ Complex __ Organic Liq.

ESD: ________ ECD: ________

SUPERVISOR: TSWalsh DATE: 1/22/96

COMMENTS:

*** BMF2-00 SPECRP: SEE SPEC SS-085 FOR REPORTING REQ'MNTS. SPECCV: ANALYZE & REPORT TOC IN DUPLICATE.

CORE

DIOXIN LABORATORY CHRONICAL

DIOXIN QT BATCH# :

SAMPLE MATRIX: 1 – WATER 2 – SOIL 3 – COMPLEX 4 – OIL

HOLD DATE: DUE DATE:

ETC SAMPLE NUMBER	CLIENT ID	ETC LOGLINK	A – TYPE	ORIGINAL BATCH	SAMPLE WT. (g) VOL. (ml)	FINAL VOL. ul
A						
B						
S						
MS						
MSD						

PROCEDURES	PERFORMED BY	DATE	LOT NUMBER	CONC ug/ml	VOLUME ul	
WEIGHT OUT						
Sodium Sulfate						
Spike ISTD/SURR						
NATIVE						
JAR SHAKE						
SOXLET						
SEP FUNNEL						
MSSG Silica Gel(______X)						UPDATES
ACID WASH(______X)						QS
SWA (Alumina)						WIP
AX21 (Carbon)						DONE
PACKAGING						EHD:

Solvent	Lot No.

ANALYST'S SIGNATURE:____________________ DATE:________________

SUPERVISOR'S SIGNATURE:____________________ DATE:________________

CORE

LABORATORIES

TCLP FILTRATION LOG

% SOLIDS DETERMINATION

QC BATCH#: ____________ HOLD DATE: ____________

SAMPLE#						
LOGLINK						
A-TYPE						
WEIGHT OF SAMPLE & FILTER AFTER FILTERING						
TARED WEIGHT OF FILTER						
WEIGHT OF FILTERED SAMPLE						
INITIAL WEIGHT OF SAMPLE						
% SOLIDS						

$$\% \text{ SOLIDS} = \frac{\text{(WEIGHT OF FILTERED SAMPLE)}}{\text{(INITIAL WEIGHT OF SAMPLE)}} \times 100$$

(ALL CALCULATIONS MUST BE SHOWN BELOW)

TECHNICIAN:	SUPERVISOR:

CORE
LABORATORIES

TCLP PREP LOG (METHOD 1311) SEMI–VOLATILE ORGANICS AND METAL

QC BATCH #: ____________________

Sample ID	LOG Link	Hold Time	Pretest 1 pH	Pretest 2 Ph	Extr. Fluid	Sample Wt. (g)	Initial Filtrate	Total Volume	Leachate pH	pH before tumbling	Fraction

SET UP: ____________________

FILTERING: ____________________

SUPERVISOR: ____________________

EXTRACTION FLUID LOT #: ____________________

Start Time: ____________________

Lab Temp: ____________________

Tumbler RPM: ____________________

Stop Time: ____________________

COMMENTS:

See attached logins and Spec sheets for special requirements and instructions.

CORE
LABORATORIES

TCLP PREP LOG (METHOD 1311) VOLATILE ORGANICS (ZHE)

QC BATCH #: ____________________

SAMPLE ID	LOG LINK	TCLP HOLD DATE	SAMPLE DUE DATE	SAMPLE WGT	INITIAL FILTRATE	TOTAL VOL	FRACTION

SET UP: ____________________ START TIME: ____________________

FILTERING: ____________________ LAB TEMP: ____________________

SUPERVISOR: ____________________ TUMBLER RPM: ____________________

EXTRACTION FLUID LOT #: ____________________ STOP TIME: ____________________

COMMENTS:

See attatched logins and specsheets for special requirements and instructions.

Figure 7.12

CORE Laboratories

LABORATORY CHRONICLE: GC/MS DEPARTMENT
SEMI-VOLATILE ANALYSIS

Date: ____________ Instr.________________
GC Column: ________________
Analyst: ________________
A-Type: ________________
Tune File: ________________
Seq. File: ________________
Method File: ________________
ID File: ________________
CB File: ________________
Reviewed By/Date: ________________
Batch #s: ________________
____

Standards Updated

Date: __________ By:____________

Tape #: ______________ Inj. _____ ul

Standard	Conc ppm	Lot No.	Lot Val
Solvent	------	Lot No.	------
	------		------

R	Name	Data File	ALS #	Dil	Inj. Time	Comments	+

R: Redo / + : Plus Search

CORE Laboratories

LABORATORY CHRONICLE: GC/MS DEPARTMENT
VOLATILE ANALYSIS

Page ______ of ______

Date: __________ Instr.__________

GC Column: __________

Batch #: __________

Water/Soil: __________

A-Type: __________

Tune File: __________

Seq. File: __________

Method File: __________

ID File: __________

CB File: __________

Analyst: __________

Standards Updated:

Date: __________

By: __________

Reviewed By: __________

Date: __________

Tape # __________

Standard	Conc ppm	Lot No.	Lot Vol.
Solvent	-----	Lot No.	-----
	-----		-----

R	pH < 2 Y/N	Name	Data File	Init. vol/wt (ml/g)	M	ALS #	Dil	Inj. Time	Comments	+

R: Redo / M: Methanol Dispersion / + : Plus Search

CORE Laboratories

Figure 7.13

LABORATORY CHRONICLE: GC DEPARTMENT
SEMI-VOLATILE ANALYSIS

Date: ____________ Instr. ________________

A-Type: ________________

Column: ________________

Col. Lot: ________________

Calib File: ________________

Seq. File: ________________

Method File: ________________

ID File: ________________

Config. File: ________________

Analyst: ________________

Reviewed By/Date: ________________

Batch #s: ________________

Standards Updated
Date: ____________ By: ____________

Tape #: ________________ Inj. ______ ul

Standard	Conc ppm	Lot No.		Standard	Conc ppm	Lot No.
				Solvent	-	Lot No.
					-	

R	Name	Data File		init. ml/g	ALS #	Dil	Comments
		Detec. 1	Detec. 2				

R: Redo

CORE .aboratories

LABORATORY CHRONICLE: GC DEPARTMENT
VOLATILE ANALYSIS

Date: ____________ Instr.____________

GC Column: ____________

Batch #: ____________

Water/Soil: ____________

A-Type: ____________

Tune File: ____________

Seq. File: ____________

Method File: ____________

ID File: ____________

CB File: ____________

Analyst: ____________

Standards Updated:

Date: ____________

By: ____________

Reviewed By: ____________

Date: ____________

Tape # ____________

Standard	Conc ppm	Lot No.	Lot Vol.
Solvent	-----	Lot No.	-----
	-----		-----

R	pH < 2 Y/N	Name	Data File	Init. vol/wt (ml/g)	M	ALS #	Dil	Inj. Time	Comments

R: Redo / M: Methanol Dispersion

Figure 7.14

CORE Laboratories

SAMPLE PREPARATION LOG - METALS

BATCH # ______________________ MATRIX ______________________

Sample ID	ICP Initial	ICP Final	Furnace Initial	Furnace Final	Mercury Initial	Mercury Final
(LCS) Control						
(PB) Q -1						
(BS) Q -A1						

Matrix Spike and Duplicate Information

Sample ID						
-1						
(MS) A1						
(D) -2						

Analyst :			
Date:			

HNO3 Lot # :		HNO3 Lot # :		HNO3 Lot # :	
HCl Lot # :		H2O2 Lot # :		H2SO4 Lot # :	
H2O2 Lot # :				HCl Lot # :	
				KMn04 Lot # :	
				K2S2O8 Lot # :	

Figure 7.15

CORE Laboratories

LAB CHRONICLE - ICP

Page ________ of ________

Date: ______________________ Instrument: ________________ Analyst: ______________________

QC Batch (s): ______________________________ Matrix: ______________________

Sequence File: ______________________________

Calibration Standard Lot # : ______________________

Calibration Check Lot # : ______________________

CRI Lot # : ________________

ICSA Lot # : ________________

ICSAB Lot # : ________________

POS	SAMPLE	DIL/ELE	POS	SAMPLE	DIL/ELE	POS	SAMPLE	DIL/ELE

CORE Laboratories

LABORATORY CHRONICLE - GFAA

Date: _____/_____/_____ Instrument FN / : ______________ Analyst: ______________

QC Batch (s): ______________________ Matrix: ______________

Calibration Standards Lot # : ______________________

Calibration Check Standard Lot # : ______________________

	Element	Position	File
1			
2			
3			
4			
5			

POS	SAMPLE	LOT #	POS	SAMPLE	DIL	POS	SAMPLE	DIL
1	SXS00		15			29		
2	SASTDS10		16			30		
3	SBSTDS20		17			31		
4	SCSTDS40		18			32		
5	SDSTDS60		19			33		
6	CSFICV		20			34		
7	CBICB		21			35		
8			22			36		
9			23			37		
10			24			38	NH4H2PO4	
11			25			39	NI(NO3)3	
12			26			40	PSTSPK SOLN	
13			27			ALT	H2SO4 5%	
14			28					

Figure 7.16

CORE Laboratories

NITRATE-NITRITE

QW-Batch: ____________ Method Ref: EPA 353.2 Page ____ of _____

QC-Batch: ____________ (Colorimetric, Automated Cd-Reduction) Date: ____________

Verified: ____________ MDL: 0.1 mg/l Time: ____________

Instrument: ____________ Matrix: Aqueous Analyst: ____________

Seq #	Lab ID	pH Int.	Analyzed mg/l	Dilution Factor	Reported mg/l	Comments Calculations

Traceability

Std Lot #:____________ External Ref #:____________ Blank Spike Ref #:____________

Color Reagent #:____________ NH4Cl-EDTA #:____________

TABLE 8.1 ROUTINE IN. ﾑENT CALIBRATION SUMMARY

INSTRUMENT	MODEL	METHODS	STANDARD RANGE	PROCEDURE	FREQUENCY
Wet Chemistry					
Spectrophotometer	Technicon AA II Technicon GTPC (Auto Analyzers)	Phenolics - 420.2/9066 Chloride - 325.2/9251 Cyanide - 335.3/9012 Cyanide - USEPA CLP Nitrate - 353.2 Nitrite - 353.2 Fluoride - 4500-F-E	0.05 - 0.30 mg/L 5.0 - 200 mg/L 0.10 - 0.50 mg/L 0 - 200 mg/L 0.10 - 2.0 mg/L 0.05 - 1.0 mg/L 0.10 - 2.0 mg/L	5 point calib. 5 point calib. 5 point calib. 5 point calib. 5 point calib. 5 point calib. 5 point calib.	per batch
	Hach DR3000	COD - Hach 8000, 1979	10.0 - 150 mg/L	5 point calib.	per batch
Carbon Analyzer	Dohrmann DC80 (w/ soil furnace)	TOC - 415.1/9060	10.0 - 400 mg/L	Single point; 5 pt verification	per batch; per batch
Infrared Spectrophotometer	Perkin Elmer 1310	Petroleum Hydrocarbon - 418.1	0.5 - 40 mg/L	5 point calib.; 2 point verification	quarterly; per batch
pH Meter	Orion 501, 701	pH - 150.1/9040	4 - 10 units	3 point calib.	per batch
Conductivity Meter	YSI #32	Specific Conductance 120.1/9050	0.01 NKCL @ 1413 umhos/cm	Single point	per batch
Turbidity Meter	Hach X/R	Turbidity - 180.1	1.8 - 180 NTU	3 point calib. (Formazine); 3 point calib.	Quarterly; per batch
Turbidity Meter	Hach X/R	Sulfate - 375.4	5.0 - 150 mg/L	5 point calib.	per batch
Seta-Flash Unit	ERDCO D15F	Flash Point - 1020	27.2° C	single point p-Xylene	per batch
Tox Analyzer	Dohrmann DX20A Mitsubishi TSX-10	TOX - 9020	1.0 ug Cl	Cal. check Std	per batch; 1/8 pyrolysis
Metals					
Mercury Cold Vapor Atomic Absorption Spectrophotometer	Fisher Hg-3 Analyzer	CVAA Hg - 245.1/7470,7471/ USEPA CLP	0.2 - 10 ug/L	6 point calib.; calibration check	Initial; Every 10 samples
Graphite Furnace Atomic Absorption Spectrophotometer	Perkin Elmer 5100 with Zeeman background correction	GFAA As - 206.2/7060/CLP Se - 270.2/7740/CLP Tl - 279.2/7841/CLP Pb - 239.2/7421/CLP Cd - 213.2/7131 Cr - 218.2/7191 Sb - 204.2/7041	By Element (ug/L) 0 - 40 0 - 40 0 - 40 0 - 40 0 - 6 0 - 12 0 - 50	4 point calib.; calibration check	Initial; Every 10 samples

TABLE ι CONTINUED

INSTRUMENT	MODEL	METHODS	STANDARD RANGE	PROCEDURE	FREQUENCY
Metals continued					
ICP Atomic Emission Spectrophotometer	Jarrell Ash ICP-61E ICP-61	ICPAE	By Element (mg/L)	4 point calib.; calibration check	Initial; Every 10 samples
		Ag - 200.7/6010/CLP	0 - 0.2		
		Al - 200.7/6010/CLP	0 - 5.0		
		As - 200.7/6010/CLP	0 - 1.0		
		B - 200.7/6010	0 - 1.0		
		Ba - 200.7/6010/CLP	0 - 2.0		
		Be - 200.7/6010/CLP	0 - 0.2		
		Ca - 200.7/6010/CLP	0 - 20		
		Cd - 200.7/6010/CLP	0 - 0.2		
		Co - 200.7/6010/CLP	0 - 0.4		
		Cr - 200.7/6010/CLP	0 - 0.6		
		Cu - 200.7/6010/CLP	0 - 0.6		
		Fe - 200.7/6010/CLP	0 - 2.0		
		Mg - 200.7/6010/CLP	0 - 20		
		Mn - 200.7/6010/CLP	0 - 0.6		
		Mo - 200.7/6010	0 - 0.5		
		Na - 200.7/6010/CLP	0 - 100		
		Ni - 200.7/6010/CLP	0 - 0.6		
		K - 200.7/6010/CLP	0 - 20		
		Pb - 200.7/6010/CLP	0 - 1.0		
		Sb - 200.7/6010/CLP	0 - 1.0		
		Se - 200.7/6010/CLP	0 - 2.0		
		Sn - 200.7/6010	0 - 2.0		
		Sr - 200.7/6010	0 - 1.0		
		Ti - 200.7/6010	0 - 1.0		
		V - 200.7/6010/CLP	0 - 0.6		
		Zn - 200.7/6010/CLP	0 - 1.0		
Organics					
Tracor Gas Chromatograph	540	Purgeable Halocarbons 601	By Compound (ug/L) 0.50 - 25 1.0 - 25	5 point calib.; calibration check	Initial; Daily
		Purgeable Halocarbons 8010	1.0 - 100 ug/L	5 point calib.; calibration check	Initial; After 10 injections
		Purgeable Aromatics 602	1.0 - 100 ug/L	5 point calib.; calibration check	Initial; Daily
		Purgeable Aromatics 8020	1.0 - 100 ug/L	5 point calib.; calibration check	Initial; After 10 injections
Hewlett Packard Gas Chromatograph	5890A 5880A	Purgeable Aromatics 602	1.0 - 100 ug/L	5 point calib.; calibration check	Initial; Daily
		Purgeable Aromatics 8020	1.0 - 100 ug/L	5 point calib.; calibration check	Initial; After 10 injections

TABLE 8.1 CONTINUED

INSTRUMENT	MODEL	METHODS	STANDARD RANGE	PROCEDURE	FREQUENCY
<u>Organics continued</u>					
		Organochlorine Pesticides/PCBs 608	By Compound (ug/ml) 0.0005 - 0.20 0.0010 - 0.40 0.0050 - 2.0 0.010 - 4.0 0.020 - 8.0	5 point calib.; calibration check	Initial; Daily
		Organochlorine Pesticides/PCBs 8080	By Compound (ug/ml) 0.005 - 0.20 0.010 - 0.40 0.050 - 2.0 0.10 - 4.0 0.20 - 8.0	5 point calib.; calibration check	Initial; After 10 injections
		Organophosphorus Pesticides - 8140	By Compound (ug/ml) 0.10 - 1.60 0.05 - 0.80 0.025 - 4.0	5 point calib.; calibration check	Initial; After 10 injections
		Chlorinated Herbicides - 8150	By Compound (ug/ml) 0.50 - 10 0.10 - 2.0	5 point calib.; calibration check	Initial; After 10 injections
		Organochlorine Pesticides and PCBs USEPA CLP	By Compound (pg) 5 - 80 10 - 160 50 - 800 100, 200, 500	3 point calib; calibration check	Initial, Every 12 hours
Hewlett Packard Gas Chromatograph/ Mass Spectrometer	5995 5995A 5988 5970A 5890A	Volatiles, purge & trap 624	4 - 200 ug/L	5 point calib.; calibration check	Initial; Daily
		Volatiles, purge & trap 8240	20 - 200 ug/L	5 point calib.; calibration check	Initial; Every 12 hours
		Volatiles, heated purge & trap - 8240	10 - 50 ug/L	5 point calib.; calibration check	Initial; Every 12 hours
		Volatiles, purge & trap 524.2	1 - 20 ug/l	5 point calib.; calibration check	Initial; Every 8 hours
		Semivolatiles (extractables) - 625	By Compound (ug/ml) 10 - 160 20 - 160 80 - 160	3/5 point calib.; calibration check	Initial; Daily
		Semivolatiles (extractables) - 8270	20 - 160 ug/ml	5 point calib.; calibration check	Initial; Every 12 hours
		PCDD, PCDF, 2,3,7,8-TCDD - 8280	20 - 500 ng	5 point calib.; calibration check	Initial; Every 12 hours

TABLE 8 .ONTINUED

INSTRUMENT	MODEL	METHODS	STANDARD RANGE	PROCEDURE	FREQUENCY
<u>Organics continued</u>					
		Volatiles, purge & trap USEPA CLP	500 - 1000 ng	5 point calib.; calibration check	Initial; Every 12 hours
		Semi-Volatiles (extractables) - USEPA CLP	20 - 160 ng	5 point calib.; calibration check	Initial; Every 12 hours
Hewlett Packard High Performance Liquid Chromatography	1090 1090A	Polynuclear Aromatic Hydrocarbons - 8310	By Compound 0.25 - 5 0.5 - 10 2.5 - 50 5.0 - 100; or 0.025 - 1.0 0.05 - 2.0 0.25 - 10.0 0.5 - 20.0	5 point calib.; calibration check	Initial; Daily verification

Figure 10.1

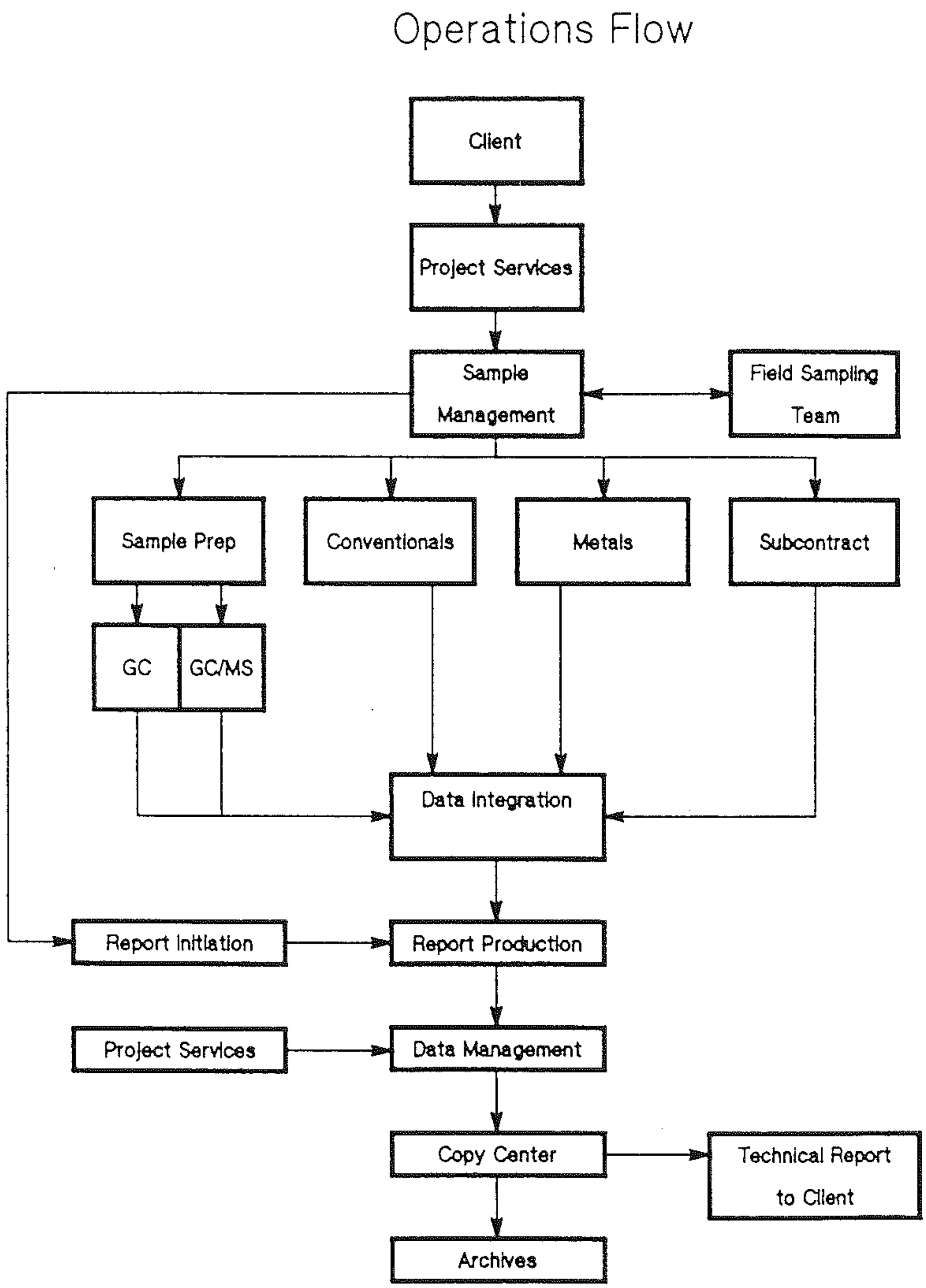

Operations Flow
Client
Project Services
Sample Management
Field Sampling Team
Sample Prep
Conventionals
Metals
Subcontract
GC
GC/MS
Data Integration
Report Initiation
Report Production
Project Services
Data Management
Copy Center
Technical Report to Client
Archives

Table 12.1

This Quality Assurance Plan (QAP) is document controlled. The table in place at the time of approval and a current list are included in order to provide updated laboratory information.

State Certification Summary
CORE LABORATORIES, INC. - EDISON, NEW JERSEY
February 29, 1996

State Agency and Certification	Laboratory ID #	Expiration
California Department of Health Services; Hazardous Waste Fields of Testing	2074	5/8/96
Connecticut Department of Health Services; Potable Water, Nonpotable Water, Soils	PH-0511	3/31/97
Massachusetts Department of Environmental Protection; Potable Water, Nonpotable Water	M-NJ136	6/30/96
New Hampshire Department of Environmental Services; Nonpotable Water	202695-B	9/25/96
New Jersey Department of Environmental Protection; Potable Water, Nonpotable Water	12005	6/30/96
New York Department of Health; Potable Water, Nonpotable Water, Hazardous Waste	10586	4/1/96
Pennsylvania Department of Environmental Resources; Potable Water	68-323	7/1/96
South Carolina Department of Health and Environmental Control; Nonpotable Water, Solid and Hazardous Waste	94002	4/1/96
Tennessee Department of Health; Potable Water	02915	10/15/98
Virginia Department of General Services; Potable Water	00113	6/30/96
Wisconsin Department of Natural Resources; Nonpotable Water	999464070	6/30/96

List of Actual Certified Tests/Parameters Available Upon Request

Table 12.1 State Certification Summary

January 30, 1996

State Agency/Certification Type	Certification ID No.
California Department of Health Services/ Hazardous Waste Fields of Testing	2074
Connecticut Department of Health Services/ Potable Water, Non-potable Water, Soils	PH-0511
Massachusetts Department of Environmental Protection/ Potable Water, Non-potable Water	M-NJ136
New Hampshire Department of Environmental Services/ Non-potable Water	202695-A
New Jersey Department of Environmental Protection/ Potable Water, Non-potable Water	12005
New York Department of Health/ Potable Water, Non-potable Water, Hazardous Waste	10586
Pennsylvania Department of Environmental Resources/ Potable Water	68-323
South Carolina Department of Health and Environmental Control/ Non-potable Water, Solid and Hazardous Waste	94002
Tennessee Department of Health/ Potable Water	02915
Virginia Department of General Services/ Potable Water	00113
Wisconsin Department of Natural Resources/ Non-potable Water	999464070

List of Actual Certified Tests/Parameters Available Upon Request

Figure 15.1

CORE Laboratories

ROUTINE CORRECTIVE ACTION LOG

Batch #: ________________ Analysis: ________________ Matrix: ________________

Preparation by: ________________________________

Analyzed by: ________________________________

Data Reviewer: ________________________________

DATE	ISSUE / RESOLUTION

Figure 15.2

For Interim Use - Core Laboratories, Inc., Edison, New Jersey - January, 1996

PACE/NJ

INVESTIGATION / CORRECTION LOG

Log #: ____________ QA Receipt Date: ____________

Originator: ____________ Date: ____________

Requested by: Pace/NJ _____ Client _____ Other _____ Resolution required by (date): ____________

Sample Information (Complete only if sample specific):

Company: ____________

Contact: ____________ Phone: ( ) ____________ Fax: ( ) ____________

Sample #s: ____________

Client ID #s: ____________

Loglink: ____________ BATCH #:

	Yes	No	Circle One	Completed by	Date
Client to be contacted?					
Corrected report(s) to be issued?			Mail/FedEx		
Letter to be issues?			Mail/Fax		
Other: ____________					

Description: ____________

Who should investigate? QA _____ Mktg _____ PM _____ Ops (Specify Dept): ____________

Investigation: ____________

Performed by: ____________ Date: ____________

QA Review / Notification of Originator / Action Taken or Required: (Check Action Type)

Name: (If applicable) ____________ Date: ____________

_____ No Action (Example: Investigation reveals no error)

_____ Simple Correction Action (Example: Correct data and reissue report)

Description: ____________

_____ Complex Correction Action (Example: Change of process, equipment)

Description: ____________

Assigned to: ____________ Date: ____________

Completed by: ____________ Date: ____________

Verified by Area Supervisor: ____________ Date: ____________

Monitored by QA: ____________ Date: ____________

N/A = Not Applicable

ATTACH SUPPORTING DOCUMENTATION

PACE/NJ 10/14/94 Rev. 0

APPENDIX C

Chemical Waste Management

Vickery, Ohio

ENSR

Evaluation of Impacts of an Acidic Material Spill on Aquatic Communities in Little Raccoon and Raccoon Creeks

ENSR Consulting and Engineering

August 1993

Document Number 1413-013-600

1413-013-600

EVALUATION OF IMPACTS OF AN ACIDIC MATERIAL SPILL ON AQUATIC COMMUNITIES IN LITTLE RACCOON AND RACCOON CREEKS

Prepared for

CHEMICAL WASTE MANAGEMENT
Vickery, Ohio

Prepared by

ENSR CONSULTING AND ENGINEERING
Fort Collins, Colorado

August 1993

CONTENTS

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(Cont'd)

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

Chemical Waste Management's Vickery Facility in Vickery, Ohio, reported a release of acidic waste into Meyer's Ditch on April 22, 1993. The release was detected at about 10:50 a.m., when a flange on a low-pressure pipeline to one of the wells was discovered to be leaking acidic material onto the ground and into an adjacent intermittent drainage ditch (Meyer's Ditch). The exact volume of waste released from the pipeline is unknown, although it was considered to be small, since a routine inspection of the line on Thursday morning (April 22) indicated no leakage. After discovering the leak, immediate actions were taken to shut off the flow and contain the acid material. On-site activities consisted of pumping the water out of Meyer's Ditch. All cleanup activities were approved by the Ohio Environmental Protection Agency (Ohio EPA). Silt screens also were established in Meyer's Ditch downstream of the facility boundary, and two downstream receiving waters, Little Raccoon and Raccoon Creeks. Initial measurements in Meyer's Ditch on April 22 indicated a low pH. As the material moved downstream, the pH increased due to dilution from the larger volume of water. By April 23 the pH had returned to about 7 in Meyer's Ditch. The release of the acidic material is believed to have caused an orange/red precipitate in the streams, possibly as a result of metals becoming insoluble in the higher pH waters of Little Raccoon Creek. The presence of orange/red water was used to track the progress of the material in Little Raccoon and Raccoon Creeks. It is believed by April 24, the material had progressed to Lake Erie. An orange precipitate was evident on the stream bottom and banks in Meyer's Ditch and Little Raccoon Creek. The orange precipitate was not obvious in Raccoon Creek.

The Raccoon Creek drainage that received the acidic material is a low-gradient, low-order stream system that drains into Lake Erie. Meyer's Ditch, which first received the acidic material, is a small, intermittent stream. The acidic material traveled about 1.5 miles in Meyer's Ditch and entered Little Raccoon Creek, which is a small, perennial stream. From its confluence with Meyer's Ditch, Little Raccoon Creek traverses about 3 miles and empties into Raccoon Creek, which is a medium-sized perennial stream that drains into Lake Erie. The approximate distance from the confluence of Little Raccoon and Raccoon Creeks to Lake Erie is about 2 miles.

The purpose of this report is to describe studies that were used to evaluate the impacts of the acidic material on aquatic communities in Little Raccoon and Raccoon Creeks. The types of studies conducted for this assessment included water and sediment chemical analyses, water and sediment toxicity, fish kill counts, and benthic macroinvertebrate and fish population surveys. The report is divided into Methods (Chapter 2.0), Results (Chapter 3.0), Discussion (Chapter 4.0), Conclusions (Chapter 5.0), and References (Chapter 6.0). In designing the studies, guidance documents (Ohio EPA 1987) regarding methods for determining biological criteria for the Ohio water bodies were reviewed. Where applicable, sampling methods and data analyses proposed for fish and macroinvertebrate studies in this plan followed the Ohio EPA (1987) biological procedures.

2.0 METHODS

2.1 Sampling Locations

Six sampling locations were selected for the chemistry and biological surveys conducted in Meyer's Ditch, Little Raccoon Creek, and Raccoon Creek (Figure 2-1). As described in Section 2.2, the types of analyses and surveys conducted at these locations varied. The approximate locations of the sampling sites are shown in Figure 2-1 and described below:

- M-1 is located in Meyer's Ditch approximately 75 yards upstream of the confluence with Little Raccoon Creek.

- US-1 is located in Little Raccoon Creek about 20 yards upstream of the confluence of Meyer's Ditch and Little Raccoon Creek. Because this site is upstream, and not influenced by inputs from Meyer's Ditch, data from this location served as a reference to data resulting from the downstream locations.

- Three locations in Little Raccoon Creek (DS-1, DS-1A, and DS-2) were sampled downstream of Meyer's Ditch. DS-1 is located immediately downstream of the confluence with Meyer's Ditch, while DS-1A is positioned about midway between the confluences with Meyer's Ditch and Raccoon Creek. DS-2 is located about 50 feet upstream of the confluence of Little Raccoon and Raccoon Creeks.

- DS-3 is in Raccoon Creek approximately 1 mile downstream of its confluence with Little Raccoon Creek. This location was the farthest downstream point that could be reached by land on April 23, and it was near the estimated downstream location of the reddish precipitate reported to be caused by the acidic material spill.

A summary of width, depth, and substrate characteristics at these six sampling locations is provided in Table 2-1.

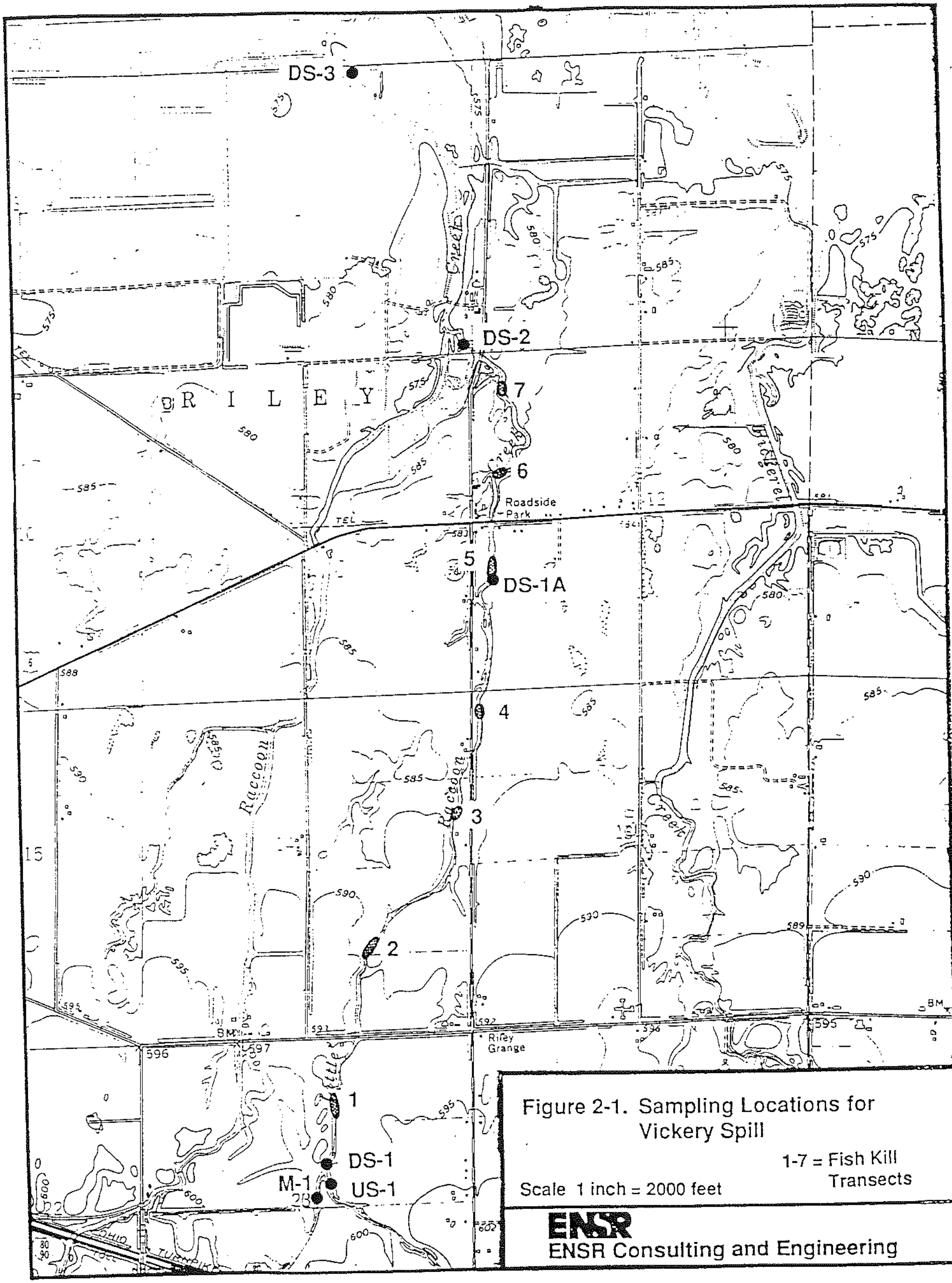


Figure 2-1. Sampling Locations for Vickery Spill

Table 2-1

Description of Sampling Locations on April 24, 1993, for the Acidic Material Leak Near the Vickery, Ohio, Facility

Location Designation	Stream Name	Width (ft)[1]	Depth (ft)[1]	Dominant Substrate
US-1	Little Raccoon Creek	4 - 6	<0.1 - 1	Silt and clay with some sand
DS-1	Little Raccoon Creek	4 - 6	<0.1 - 1.5	Silt and sand
DS-1A	Little Raccoon Creek	4 - 10	<0.1 - 3	Clay and detritus
DS-2	Little Raccoon Creek	18 - 25	0.5 - 4	Clay and detritus
DS-3	Raccoon Creek	40 - 50	2 - 6	Clay and silt
M-1	Meyer's Ditch	3 - 4	<0.1 - 0.2	Silt and clay

[1]Width and depth fluctuated during the three sampling periods.

2.2 Types of Analyses and Surveys

The types of analyses and surveys conducted for the acidic material leak assessment included water and sediment chemistry, water and sediment toxicity, fish kill survey, benthic macroinvertebrate sampling, and fish population sampling. The initial studies consisted of water and sediment chemistry, collection of water for toxicity testing, and a fish kill survey. These studies were conducted on April 23 and 24, 1993, which was within 48 hours following the detection of the pipeline leak. Subsequent collections and biological surveys were conducted on April 29, May 13, and June 2 and 3, 1993, as indicated in Table 2-2. The types of analyses and surveys conducted at the six sampling locations also are listed in Table 2-2. The April 29 analyses (water and sediment chemistry and collection of water for toxicity testing) were included to determine the effects of a heavy rain event on April 25 and 26, 1993.

2.3 Chemistry

Water samples for analytical chemistry (metals) were collected in clean, high-density polyethylene containers (Eagle-Picher®). The containers were rinsed with stream water and then filled. The samples were kept on ice (at or near 4° C) until arrival at the laboratory (Aquatech, Marion, Ohio). At the laboratory the samples were filtered through a 0.45 µm filter to obtain samples for dissolved measurements. Water samples from the first sampling effort (April 23 to 24) were not analyzed for total metals (prior to filtration); samples collected during the second and third sampling efforts were analyzed for dissolved and total metals. Analysis was completed using EPA method 200.7/6010 (Inductively Coupled Plasma Emission - ICP). Samples were analyzed for 22 metals (see Chapter 3.0, Results).

Sediment samples were collected by scooping material from the stream bottom by hand with heavy, rubber gloves. At each site the gloves were thoroughly cleaned with site water, prior to collection of the sample. Samples were placed in wide-mouth, high-density polyethylene jars or Ziploc® bags. Sediment samples were kept on ice (at or near 4°C) until analysis at the laboratory (Aquatech, Marion, Ohio). Sediment samples were analyzed for the same metals as the water samples, also using ICP, following digestion. All analytical samples were labeled with the site designation, stream name, date, and type of sample.

Duplicate water and sediment samples were collected. Data were analyzed by determining the mean value of each parameter. If a metal concentration for one duplicate was below the method detection limit, but the other duplicate had a detectable concentration, then the below detection duplicate was assigned a value of 1/2 the detection limit.

Tabl 2

Samples Collected and Analyses Performed at Selected Sites
Near the Vickery, Ohio, Facility

Site	Dates	Water Chemistry	Sediment Chemistry	Water Toxicity	Sediment Toxicity	Fish Kill Survey[1]	Benthic Population Survey	Fish Population Survey
US-1	April 23-24	X	X	X		X		
US-1	April 29-30	X	X					
US-1	May 13			X				
US-1	June 2-3	X	X		X		X	X
DS-1	April 23-24	X	X	X		X		
DS-1	April 29-30	X	X					
DS-1	May 17			X				
DS-1	June 2-3	X	X		X		X	X
DS-1A	June 2-3	X	X				X	X
DS-2	April 23-24	X	X	X		X		
DS-2	April 29-30	X	X					
DS-2	May 13			X				
DS-2	June 2-3	X	X				X	X
DS-3	April 23-24	X	X	X		X		
DS-3	April 29-30	X	X					
DS-3	May 13			X				
DS-3	June 2-3	X	X		X			
M-1	April 23-24		X			X		
M-1	April 29-30	X	X					

[1] Fish kill surveys were actually completed by counting dead fish in several sections of the impacted creeks.

2.4 Biological

The health of aquatic ecosystems, either under normal conditions or following an acute impact, is typically assessed using analytical chemistry and toxicity tests. These aspects of this study have been addressed in Sections 2.3 and 2.5. The Ohio EPA recommends targeted sampling of both the fish and benthic macroinvertebrate communities (Ohio EPA 1987). Fish and macroinvertebrates inhabit receiving waters continuously and are a reflection of the chemical, physical, and biological history of the receiving waters. The Biological Criteria documents (Volumes 1 through 3) are designed to examine the continuous conditions of a water body, and do not specifically address impacts of an unanticipated spill (Ohio EPA 1987). Therefore, some methodologies suggested are not applicable to the Vickery spill (e.g., use of artificial substrates for the collection of benthic macroinvertebrates).

2.4.1 Fish Kill Survey

Fish kill surveys were conducted in Meyer's Ditch, Little Raccoon Creek, and Raccoon Creek on April 23 and 24. The method used to count dead fish varied depending on the size and length of the three streams, as well as access restrictions. Since Meyer's Ditch was relatively small and the length affected by the leak was about 1.5 miles, the lower 1 mile of this stream was walked on April 22 and examined for dead fish. In contrast, Raccoon Creek was surveyed by boat because the stream was quite deep and shoreline access was limited. The entire shoreline area was surveyed for dead fish along both banks from its confluence with Little Raccoon Creek and Lake Erie.

The counting method used in Little Raccoon Creek was a transect procedure recommended for narrow streams by the American Fisheries Society (1982). The procedure involved dividing the 3-mile study area in Little Raccoon Creek into 0.5-mile sections. Initial measurements on-site estimated the Little Raccoon segment to be about 3.5 miles. Subsequent, more accurate measurements indicated the segment was 3.0 miles. Therefore, all dead fish were counted in one 100-yard segment within each 0.5-mile section in the upper 2.5 miles of Little Raccoon Creek; and two segments in the lower portion of the creek (just upstream of its confluence with Raccoon Creek). The initial 100-yard segment was randomly selected in the downstream portion of the stream. Subsequent 100-yard segments were selected at approximate 0.5-mile intervals. The exact location of the segments also depended on landowner's permission. In total, seven 100-yard segments were counted for dead fish (numbered 1 through 7 in Figure 2-1). All dead fish within each 100-yard segment were counted on April 24 by walking the streambanks. The numbers and length of fish were recorded in a field notebook. The total fish counts for the seven, 100-yard segments were expanded to the entire 3.0 miles in Little Raccoon Creek by the following formula:

$$E = (1{,}760 \text{ yards/mile}) \; T/L$$

Where: E = expansion factor
T = total length affected by leak (3.0 miles)
L = sum of the lengths of the counting segments (700 yards).

The expansion factor was multiplied by the counts for each species to estimate the total number of dead fish for the 3.0 miles in Little Raccoon Creek.

On the initial day of the leak and during the fish kill counts, dead fish were collected and frozen for potential use in tissue analyses. The fish are being held at ENSR's laboratory in Fort Collins.

2.4.2 Benthic Macroinvertebrates

Benthic macroinvertebrates are those organisms living in or on the substrate of a lake or, in this case, a stream. These organisms can be insects (e.g., midge larvae) or other invertebrates (e.g., crayfish or worms). In order to assess the impacts on the benthic community, quantitative samples were obtained from the four sites in Little Raccoon Creek within approximately 5 weeks of the material leak. These sites included US-1, DS-1, DS-1A, and DS-2.

At each site, four replicate samples were collected using a petite Ponar dredge (grab). The grab samples were placed into a bucket with a brass grid in the bottom; large rocks or other debris were checked for organisms and removed. Excess sediment was rinsed out of the bottom of the bucket. All captured organisms and remaining debris were placed in a wide-mouth jar and preserved with 5 to 10 percent buffered formalin.

In the laboratory, all samples were picked and sorted, and organisms placed in 70 percent isopropanol. Identification and enumeration of macroinvertebrates were performed by Mr. Henry Zimmerman, a taxonomist located in Fort Collins, Colorado. Organisms will be identified to the Lowest Practical Taxon (LPT). Community parameters calculated for this study include: density ($\#/m^2$), number of taxa, Shannon diversity, and Shannon evenness (Shannon diversity and evenness were calculated using the natural log). In addition to these parameters, the Invertebrate Community Index (ICI) also was computed according to Ohio EPA (1987). Statistical analyses were performed on densities, number of taxa, Shannon diversity, and evenness at the upstream and downstream locations using analysis of variance and Tukey's multiple range test ($\alpha = 0.05$).

2.4.3 Fish Population Survey

A fish survey was conducted on June 2, 1993, to determine the relative impact of the leak on fish composition and relative abundance. Since most of the dead fish were observed in Little Raccoon Creek, this stream was emphasized in the survey. Four sample locations were surveyed in Little Raccoon Creek, which included upstream of the confluence with Meyer's Ditch (reference site, US-1), downstream of the confluence with Meyer's Ditch (DS-1), upstream of the Route 6 Bridge (DS-1A), and about 100 feet upstream with the confluence with Raccoon Creek (DS-2). The survey was conducted using a backpack electroshocker (Smith-Root) in a 100-foot section at each location. A two-pass removal method was used to estimate fish numbers at each location (Seber and LeCren 1967). Equal effort was used for each pass at each site.

The following equation was used for estimating populations of the most abundant species (or taxonomic groups, i.e., minnows) and total fish at each site:

$$N = \frac{U_1}{1-(U_2/U_1)}$$

Where: N = population estimate;
U_1 = number of fish removed on the first pass; and
U_2 = number of fish removed on the second pass.

For comparative purposes, abundance data were expressed as a consistent density measure (e.g., fish per acre [ac]). The estimated probability of capture (p) on each pass was calculated for estimated populations using the following equation:

$$p = 1-(U_2/U_1)$$

Probability of capture values in this study varied depending upon the sampling location. Sampling at US-1 showed a probability of capture of 1, while values at the other locations were 0.67 at DS-1, 0.73 at DS-1A, and 0.72 at DS-2. Probability of capture values less than 0.80 indicate that, because of lower sampling efficiency, the population estimate is of lower accuracy.

Three biologists electrofished the stream by walking slowly upstream and collecting any stunned fish. All fish were identified and enumerated; non-minnow species, such as white sucker or green sunfish, were measured for total length in millimeters and weighed in grams. All fish were examined externally for evidence of disease or parasites. All fish were returned to the stream after field processing. The number and percent composition of fish were presented for each location. To allow useful comparisons to the reference site, the effort at each site was the same, especially in terms of the length of the sampling.

In conjunction with the fish sampling, a general characterization of macrohabitat features was made at the four sampling locations following the Ohio EPA's (1987) Qualitative Habitat Evaluation Index (QHEI) procedure. The QHEI requires data on substrate, instream cover, channel morphology, riparian zone and bank erosion, pool or riffle quality, and riffle/run depth. The reason for including the QHEI with the fish survey was to document whether habitat characteristics are contributing to possible differences in fish communities at the four sampling locations.

2.5 Toxicity Testing

2.5.1 Water

Samples for toxicity testing were collected in new, 2.5-gallon cubitainers (two from each site), which were rinsed with site water before being filled. The cubitainers were labeled appropriately and kept on ice at or near 4°C until arrival at ENSR Consulting and Engineering's Fort Collins Environmental Toxicology Laboratory (FCETL) in Fort Collins, Colorado. Upon arrival, the samples were logged in and stored at 4°C until initiation of toxicity testing. For each of the four samples, chronic tests were performed using the water flea (*Ceriodaphnia dubia*) and the fathead minnow (*Pimephales promelas*). The tests were conducted using standard U.S. Environmental Protection Agency (EPA) (1989) methods.

Due to a shipping error, water from site DS-1 was not collected on May 13 for the second round of toxicity testing along with water from the other sites. Water from this site was collected on May 17 and shipped to the FCETL.

At the end of the testing period (7 days for *Pimephales promelas* and 5 to 8 days for *Ceriodaphnia dubia*, depending on organism reproductive performance), data were analyzed using appropriate parametric or nonparametric statistical methods ($\alpha=0.05$) depending on whether the data met normality and variance assumptions ($\alpha=0.01$). Parameters calculated include: 48-hour LC_{50}, NOEC, and IC_{25}. The 48-hour LC_{50} is an acute endpoint that measures the Lethal Concentration at which 50 percent of organisms die after 48 hours. The NOEC is the No Observable Effect Concentration, and is the concentration at which there is no significant difference from the control at the end of a chronic test. Finally, the IC_{25} is the Impact Concentration representing the concentration at which there is a 25 percent reduction in organism performance at the end of a chronic test.

2.5.2 Sediment

To determine if sediments downstream of Meyer's Ditch display significantly greater toxicity than upstream sediments, toxicity tests were performed using the amphipod, *Hyalella azteca*. Sediments were collected at US-1, DS-1, and DS-2 in clean, 4-liter jars to correspond with the biotic sampling (on June 3). The sediment samples were labeled appropriately, placed on ice, and shipped to the FCETL in Fort Collins, Colorado. Testing was conducted on 100 percent stream sediment and a reference sediment using the American Society of Testing and Materials (ASTM) standard methods (1992). The endpoints examined were organism survival and significant difference from the reference sediment (a clean, laboratory sediment) and upstream control sediment (US-1).

3.0 RESULTS

3.1 Chemistry

3.1.1 Water

Several parameters were not detected in the water samples in either their total or dissolved forms: aluminum, barium, calcium, iron, potassium, magnesium, manganese, sodium, and zinc (Table 3-1). The lack of detectable levels of metals, however, may be due more to the method detection limit than to the actual absence of the material in the water. The method detection limit for several metals using ICP is higher than what could be detected using other techniques and, in fact, is higher than levels that may produce toxic responses. For example, the detection limit for selenium was 70 $\mu g/L$ using ICP. However, the EPA acute and chronic criteria (EPA 1991) for the protection of aquatic life are 20 and 5 $\mu g/L$, respectively. Therefore, selenium could still be present in the water column at toxic levels, but not be detected using ICP. High levels of some metals in the sediment (see Section 3.1.2) support this possibility. Discussion, however, will be limited to those materials that were detected in the water column. In some cases, total concentrations were higher than dissolved forms; for most parameters, however, there was little difference between dissolved and total forms, indicating that much of the material was bioavailable. Because it is the dissolved form that is bioavailable and thus potentially toxic, discussion will be further limited to dissolved concentrations.

For several metals the EPA chronic and acute criteria were calculated and compared to measured concentrations. Since metal toxicity is often related to the hardness of the water, with toxicity decreasing with increasing hardness, it was necessary to calculate site-specific metal criteria for manganese, lead, and zinc. Samples collected on April 23 showed hardness values ranging from 382 to 452 mg/L as $CaCO_3$. Samples collected on May 13 showed higher hardness values, ranging up to 680 mg/L. These values were similar to what was measured by Chemical Waste Management . Since hardness of the stream water at the time of the spill was probably closer to the April values, criteria were calculated using a hardness of 400 mg/L as $CaCO_3$ to represent an average of the various measurements.

Zinc. Zinc was one of only two metals measured at very high concentrations during the first sampling period (Figure 3-1). The measured concentration at DS-2 was nearly 3 mg/L dissolved zinc, and the concentration at DS-3 was nearly 2 mg/L. There were also detectable levels of zinc at both US-1 and DS-1, although these levels were below both the acute and chronic criteria.

Table 3-1

Mean Concentrations (ppm) of All Analytes

Station	Date	Matrix	Form	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg
US1	Apr 23	Water	Diss	0	0	0	0.04	0	117	0	0	0	0	0	0
US1	Apr 29	Water	Diss	0	0.08	0	0.035	0	128.5	0	0	0	0	0	0
US1	Jun 03	Water	Diss	0	0.19	0	0.049	0	214.5	0	0	0	0	0.142	0
US1	Apr 29	Water	Total	0	0.735	0	0.04	0	135	0	0	0	0	0.51	0
US1	Jun 03	Water	Total	0	0.435	0	0.054	0	227.5	0	0	0	0	0.332	0
US1	Apr 23	Sediment	Total	0	8400	92	64.5	0.45	12935	0.7	13	10	15.5	19450	0
US1	Apr 29	Sediment	Total	0	6250	0	56	0.325	11500	0	13.5	10	14	17500	0
US1	Jun 03	Sediment	Total	0	6055	15	62.5	0.45	6400	0	13.5	9.5	12.5	15350	0
DS1	Apr 23	Water	Diss	0	0	0	0.03	0	109	0	0	0	0	0	0
DS1	Apr 29	Water	Diss	0	0	0	0.03	0	124.5	0	0	0	0	0	0
DS1	Jun 03	Water	Diss	0	0.195	0	0.048	0	211.5	0	0	0.007	0	0.193	0
DS1	Apr 29	Water	Total	0	0.745	0	0.04	0	137	0	0	0	0	0.525	0
DS1	Jun 03	Water	Total	0	0.455	0	0.052	0	218	0	0	0	0	0.365	0
DS1	Apr 23	Sediment	Total	0	6745	120	70	0.55	7200	0	12	26.5	17.5	21100	0
DS1	Apr 29	Sediment	Total	0	10850	0	145	0.7	8800	0.525	32	21	23.5	28850	0.04
DS1	Jun 03	Sediment	Total	0	10575	37	162.5	0.85	13950	0.275	30.5	15	75	36300	0.035
DS1A	Jun 03	Water	Diss	0	0.345	0	0.053	0	210	0	0	0	0	0.408	0
DS1A	Jun 03	Water	Total	0	0.515	0	0.072	0	254	0	0	0	0	0.495	0
DS1A	Jun 03	Sediment	Total	0	13450	20	75	0.8	34050	0	11	71	23	21250	0.095
DS2	Apr 23	Water	Diss	0	0	0	0.035	0	104.5	0	0	0	0	0	0
DS2	Apr 29	Water	Diss	0	0.12	0	0.05	0	108	0	0	0	0	0	0
DS2	Jun 03	Water	Diss	0	0.37	0	0.041	0	183.5	0	0	0	0	0.466	0
DS2	Apr 29	Water	Total	0	2.745	0	0.05	0	99.3	0	0	0	0	3.235	0
DS2	Jun 03	Water	Total	0	1.015	0	0.046	0	193	0	0	0	0	0.859	0
DS2	Apr 23	Sediment	Total	0	17350	174	111	1.05	6350	0	16.5	20	21.5	32300	0
DS2	Apr 29	Sediment	Total	0	12500	10	89	0.85	10400	0	19.5	23.5	21.5	31150	0.085
DS2	Jun 03	Sediment	Total	0	17550	28.75	103	1.15	10265	0	18.5	24.5	26	32150	0.145

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

Table 3-1 (Continued)

Station	Date	Matrix	Form	Ag	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg
DS3	Apr 23	Water	Diss	0	0	0	0.04	0	117.5	0	0	0	0	0	0
DS3	Apr 29	Water	Diss	0	0.075	0	0.04	0	120	0	0	0	0	0	0
DS3	Jun 03	Water	Diss	0	0.58	0	0.062	0	203	0	0	0	0	0.781	0
DS3	Apr 29	Water	Total	0	1.905	0	0.04	0	111	0	0	0	0	2.465	0
DS3	Jun 03	Water	Total	0	1.06	0	0.057	0	171.5	0	0	0	0	1.365	0
DS3	Apr 29	Sediment	Total	0	8400	0	51	0	39500	0	10	13	16.5	19050	0.05
DS3	Jun 03	Sediment	Total	0	10635	22	59	0.55	40650	0	10	15	20.5	20600	0.08
M1	Apr 29	Water	Diss	0	0.08	0	0.03	0	86.3	0	0	0	0	0	0
M1	Apr 29	Water	Total	0	0.99	0	0.04	0	88.95	0	0	0	0	0.765	0
M1	Apr 23	Sediment	Total	0	12600	137	132	0.85	8500	0	30.5	18	22.5	30450	0
M1	Apr 29	Sediment	Total	0	10200	0	125	0.7	7300	0	27.5	33.5	23.5	25300	0

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

Table 3-1 (Continued)

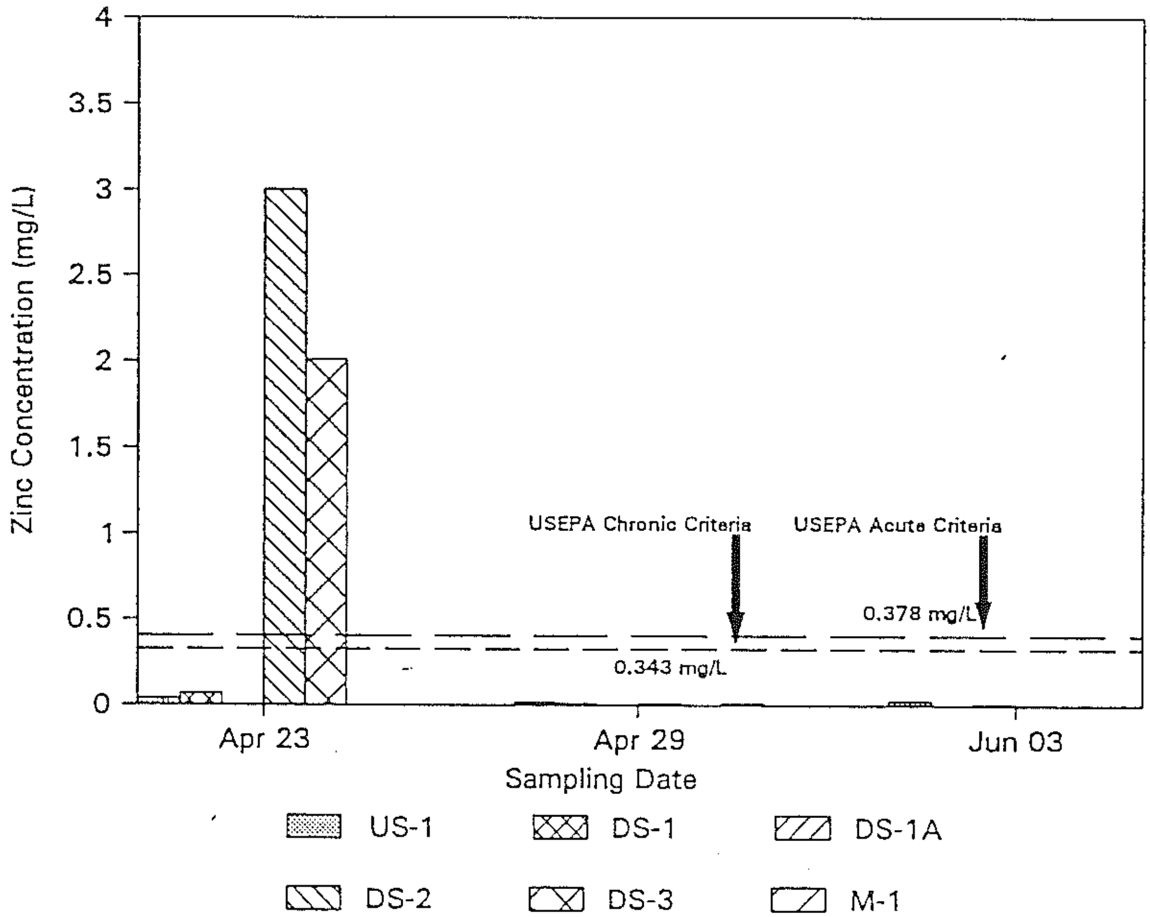
Station	Date	Matrix	Form	K	Mg	Mn	Na	Ni	Pb	Se	Sb	Tl	V	Zn
US1	Apr 23	Water	Diss	3.4	29.2	0.04	24.25	0	0	0	0	0	0	0.037
US1	Apr 29	Water	Diss	3.35	33.05	0.05	22.65	0	0.06	0	0	0	0	0.02
US1	Jun 03	Water	Diss	5.9	35.85	0.093	27.7	0	0	0	0	0	0	0.026
US1	Apr 29	Water	Total	3.5	34.7	0.06	23.55	0	0	0	0	0	0	0
US1	Jun 03	Water	Total	6	37.45	0.101	28.55	0	0	0	0	0	0	0
US1	Apr 23	Sediment	Total	795	5360	680	126.5	21.5	13	65.5	0	0	17	47.5
US1	Apr 29	Sediment	Total	700	3850	745	145	21	15	0	0	0	16	45
US1	Jun 03	Sediment	Total	821.5	2755	915.5	146.5	22.5	15	15	0	0	20	46
DS1	Apr 23	Water	Diss	3.1	29.05	0.06	24.75	0	0	0	0	0	0	0.07
DS1	Apr 29	Water	Diss	3.2	31.7	0.05	21.75	0	0.065	0	0	0	0	0.012
DS1	Jun 03	Water	Diss	5.85	35.65	0.098	27.55	0	0	0	0	0	0	0
DS1	Apr 29	Water	Total	3.8	35.3	0.06	23.8	0	0	0	0	0	0	0
DS1	Jun 03	Water	Total	6.05	36.35	0.102	28	0	0	0	0	0	0	0
DS1	Apr 23	Sediment	Total	965	4550	553.5	135	24.5	12.5	69.5	0	0	19	71.5
DS1	Apr 29	Sediment	Total	1200	4850	1900	165	44.5	35.5	0	0	0	28	95.5
DS1	Jun 03	Sediment	Total	1257	5085	2220	167.5	40	19.5	8	0	0	35	71
DS1A	Jun 03	Water	Diss	5.1	38.35	0.105	40.35	0	0	0	0	0	0	0.009
DS1A	Jun 03	Water	Total	5.05	47.8	0.138	37.4	0	0	0	0	0	0	0
DS1A	Jun 03	Sediment	Total	2400	6575	362	378.5	24	11.5	0	0	0	31	180
DS2	Apr 23	Water	Diss	3.45	27.65	0.56	26.15	0.1	0	0	0	0	0	3
DS2	Apr 29	Water	Diss	3.4	31.1	0.135	23.3	0	0.035	0	0	0	0	0.012
DS2	Jun 03	Water	Diss	5.45	31.75	0.084	46.45	0	0	0	0	0	0	0
DS2	Apr 29	Water	Total	3.45	29.25	0.155	22.25	0	0	0	0	0	0	0.03
DS2	Jun 03	Water	Total	6.1	33.25	0.092	48.45	0	0	0	0	0	0	0
DS2	Apr 23	Sediment	Total	1305	5150	330	173	31	17	109	0	0	28	80
DS2	Apr 29	Sediment	Total	1400	5700	395	310	37	25	10	8.5	10	25	116.5
DS2	Jun 03	Sediment	Total	2310	6690	388.5	250.5	36	21	8.225	0	0	42.5	109.5

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.

Table 3-1 (Continued)

Station	Date	Matrix	Form	K	Mg	Mn	Na	Ni	Pb	Se	Sb	Tl	V	Zn
DS3	Apr 23	Water	Diss	4.1	25.85	0.315	30.95	0.065	0	0	0	0	0	2.01
DS3	Apr 29	Water	Diss	3.6	27.35	0.07	30	0	0.03	0	0	0	0	0
DS3	Jun 03	Water	Diss	6.4	36.9	0.151	54.65	0	0	0	0	0	0	0
DS3	Apr 29	Water	Total	4	25.45	0.095	28.65	0	0	0	0	0	0	0.025
DS3	Jun 03	Water	Total	5.8	30.8	0.132	47.1	0	0	0	0	0	0	0.01
DS3	Apr 29	Sediment	Total	955	8000	215	335	23	12.5	0	0	0	14.5	116
DS3	Jun 03	Sediment	Total	1300	11835	240	225	23	10	4	0	0	24	63.5
M1	Apr 29	Water	Diss	1.95	34.85	0.01	23.4	0	0.195	0	0	0	0	0.012
M1	Apr 29	Water	Total	2.3	36.05	0.11	23.8	0	0	0	0	0	0	0.1
M1	Apr 23	Sediment	Total	1145	5700	1860	164	40.5	24.5	99.5	0	0	31	102
M1	Apr 29	Sediment	Total	990	4800	1650	245	42	29.5	0	0	0	24.5	135

Note: Zeros are below detection. Some nondetects were assigned a value of 1/2 the detection limit for calculation of means.



Note: Criteria are hardness dependent and calculated assuming hardness of water = 400 mg/L (as $CaCO_3$)

Figure 3-1. Mean concentration of dissolved zinc in water samples collected at six sites on three dates following the spill.

Samples collected during the second and third sampling rounds showed very low or undetectable levels of zinc.

Manganese. Like zinc, manganese concentrations in water samples collected on April 23 were much higher at DS-2 and DS-3 compared to concentrations at US-1 or DS-1 (Figure 3-2). Also, like zinc, the concentrations decreased dramatically during the second and third sampling rounds. Despite these elevated levels of manganese, the concentrations were still below the estimated criteria (acute = 2.5 mg/L; chronic = 2.1 mg/L). These criteria were calculated at ENSR using EPA methods.

Lead. Lead was the only metal measured that showed higher dissolved concentrations in samples collected during the second sampling period (April 29) (Figure 3-3). The level in the water samples collected at M-1 was in excess of 0.19 mg/L, which was well above the EPA chronic criterion of 0.0185 mg/L at a hardness of 400 mg/L. While lead concentrations at DS-1, DS-2, and DS-3 were also high, so was the dissolved lead concentration measured at US-1. Therefore, some of the lead may be coming from another source.

Aluminum. Aluminum was highest during the third sampling period (Figure 3-4), with the highest levels being found at DS-3. Concentrations at US-1 were measurable, although lower than at the other sites. Aluminum was undetectable during the first sampling period. No measured concentrations, however, were above the EPA acute and chronic criteria (for pH between 6.5 and 9.0) of 1.496 and 0.748 mg/L.

For other metals that were detected in the water column samples, concentrations were often higher in the third sampling period (e.g., iron, magnesium, sodium). This may be due to the low water conditions that resulted in a concentrating effect on ions. For most of the materials, concentrations at US-1, the upstream reference site, were neither consistently higher nor lower than at the downstream sites.

3.1.2 Sediment

Nearly all metals for which analysis was performed were detected in sediments (Table 3-1). Silver was not detected, and cadmium, antimony, and titanium were detected in only a few samples. Several metals were present at higher concentrations at the downstream sites than at the upstream reference site (US-1). Those include zinc (Figure 3-5), vanadium (Figure 3-6), and nickel (Figure 3-7). The concentration of lead at US-1 was slightly higher than at DS-1 in samples collected on April 23, but concentrations were higher at DS-2, and even higher at M-1

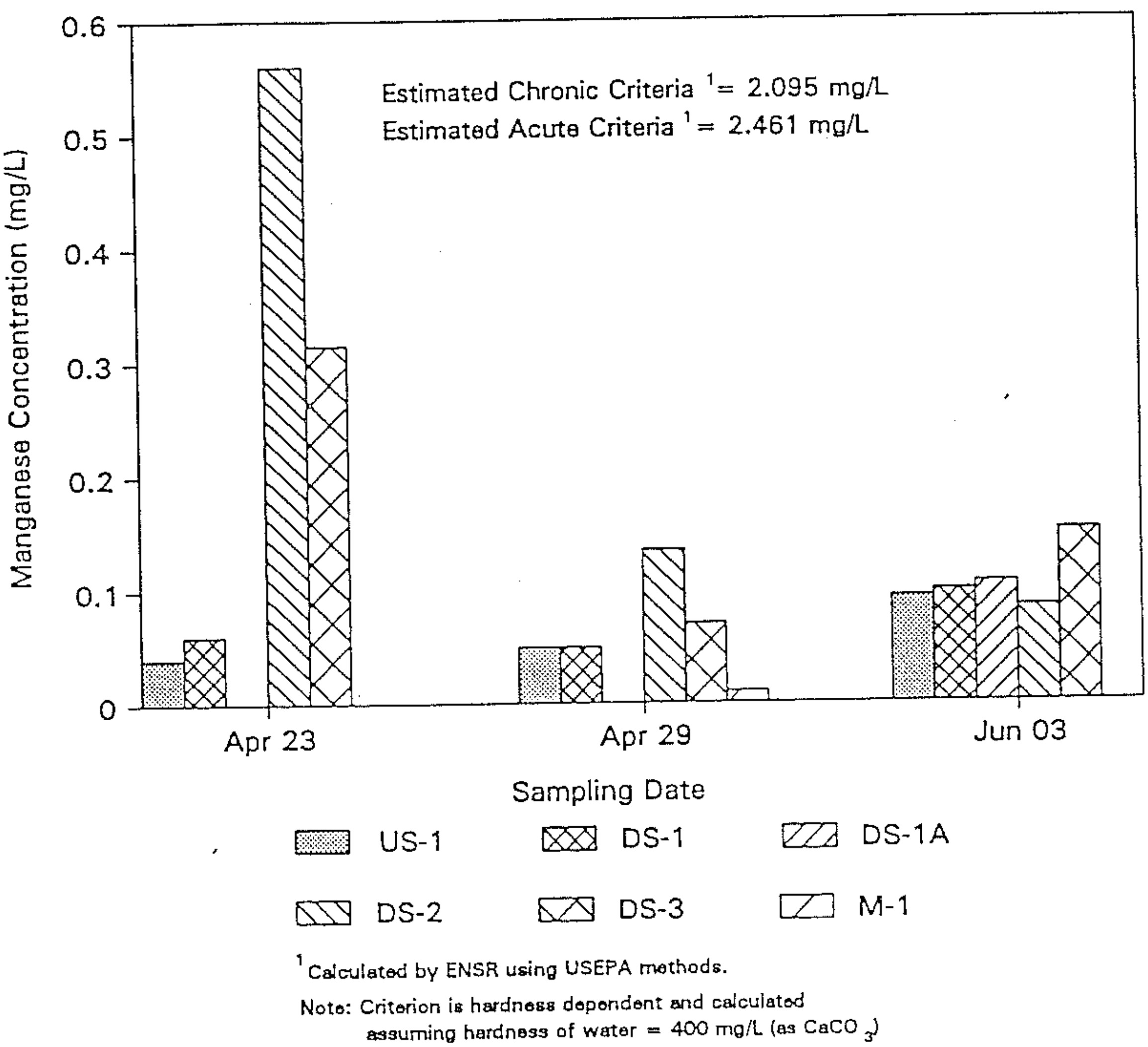


Figure 3-2. Mean concentration of dissolved manganese in water samples collected at six sites on three dates following the spill.

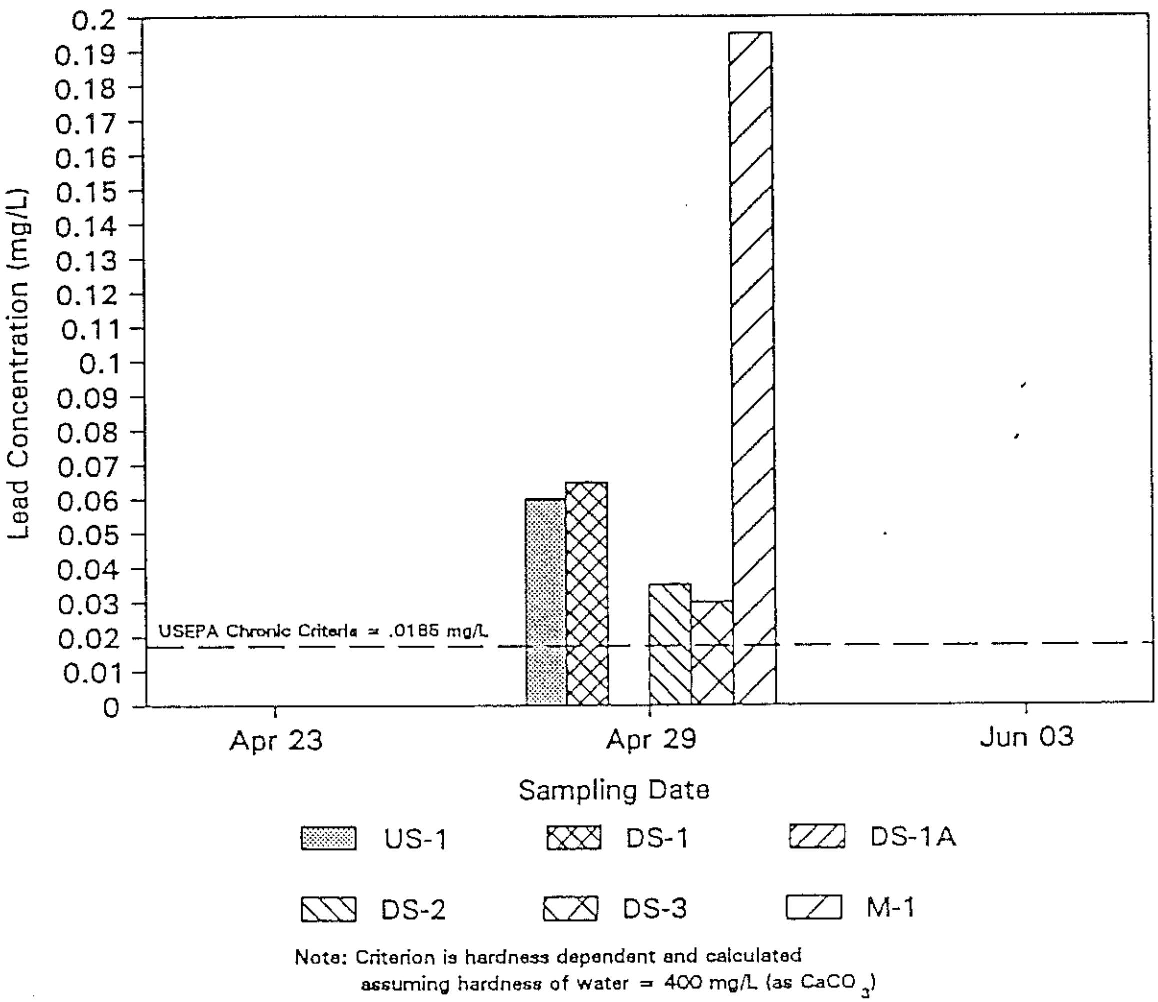


Figure 3-3. Mean concentration of dissolved lead in water samples collected at six sites on three dates following the spill.

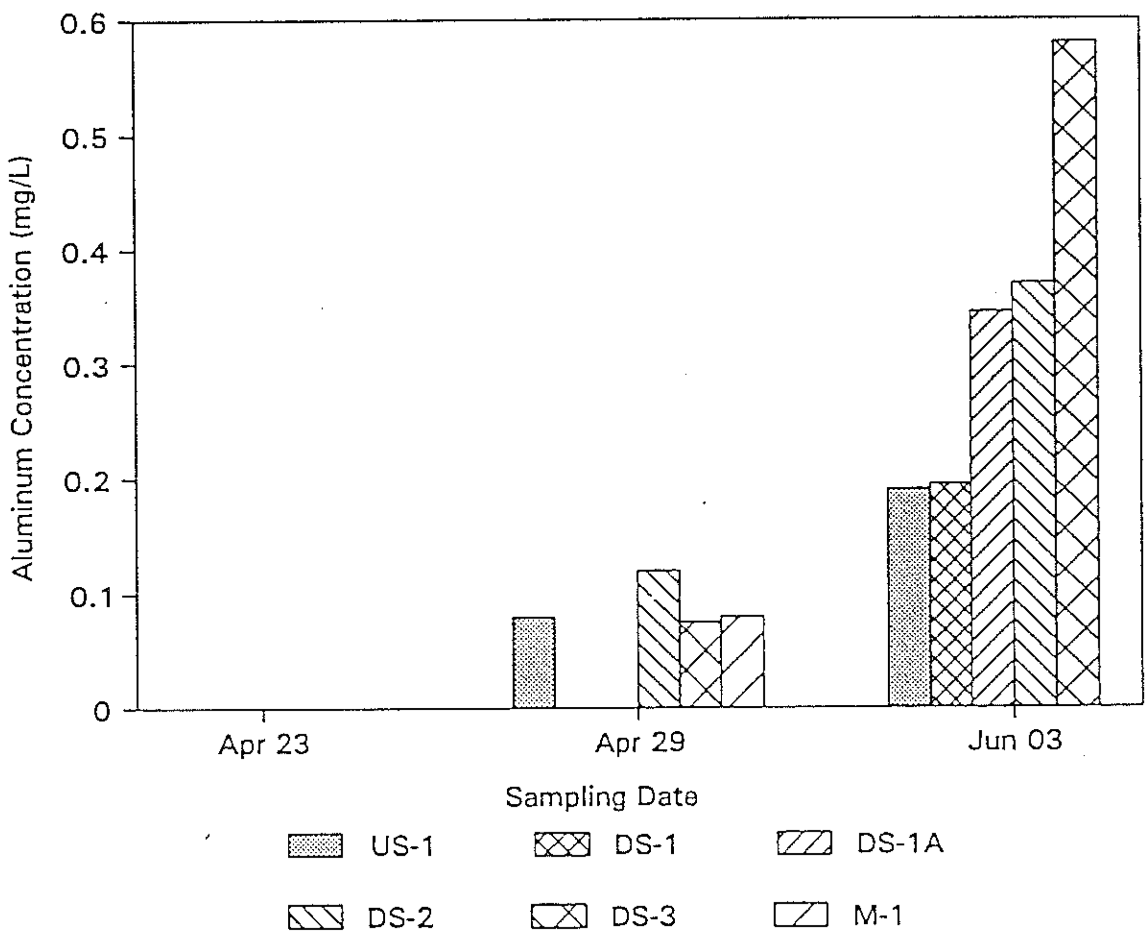


Figure 3-4. Mean concentration of dissolved aluminum in water samples collected at six sites on three dates following the spill.

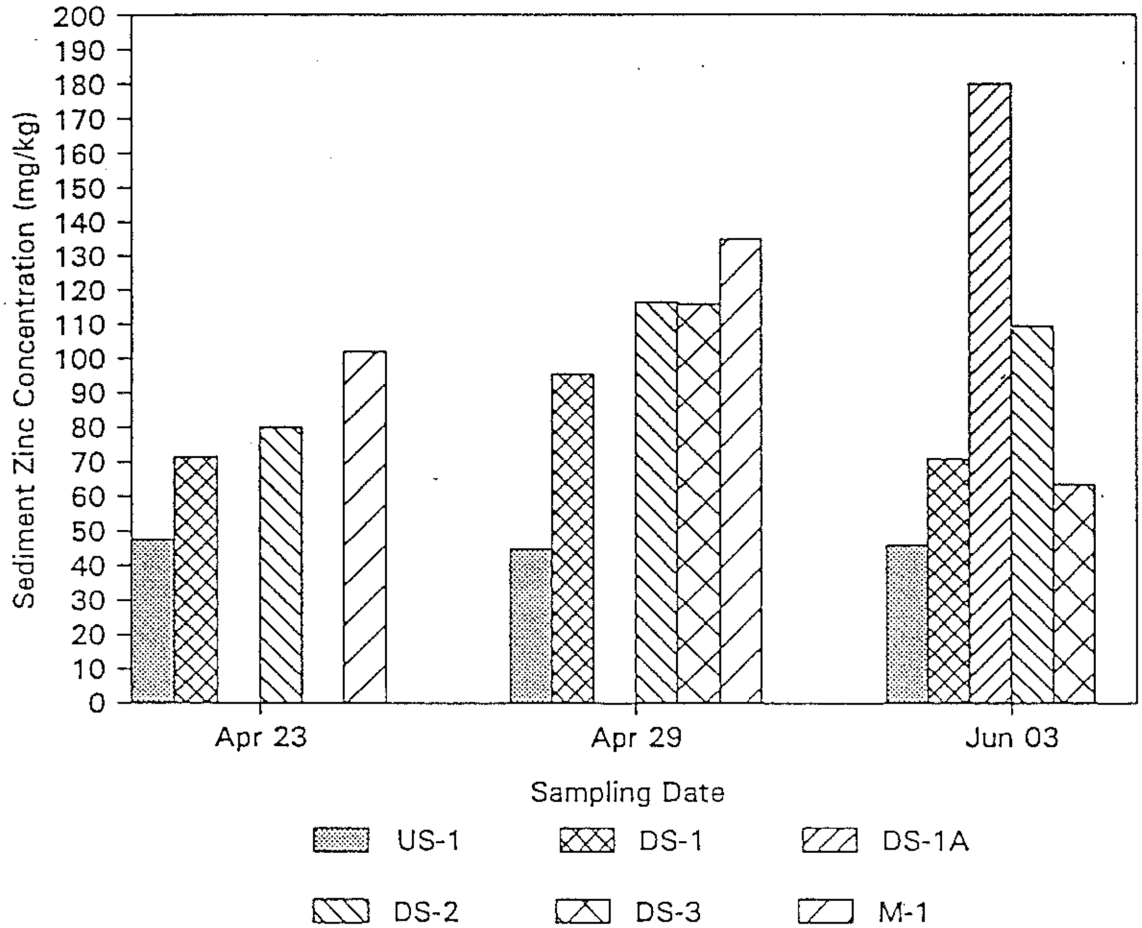


Figure 3-5. Mean concentration of zinc in sediment samples collected at six sites on three dates following the spill.

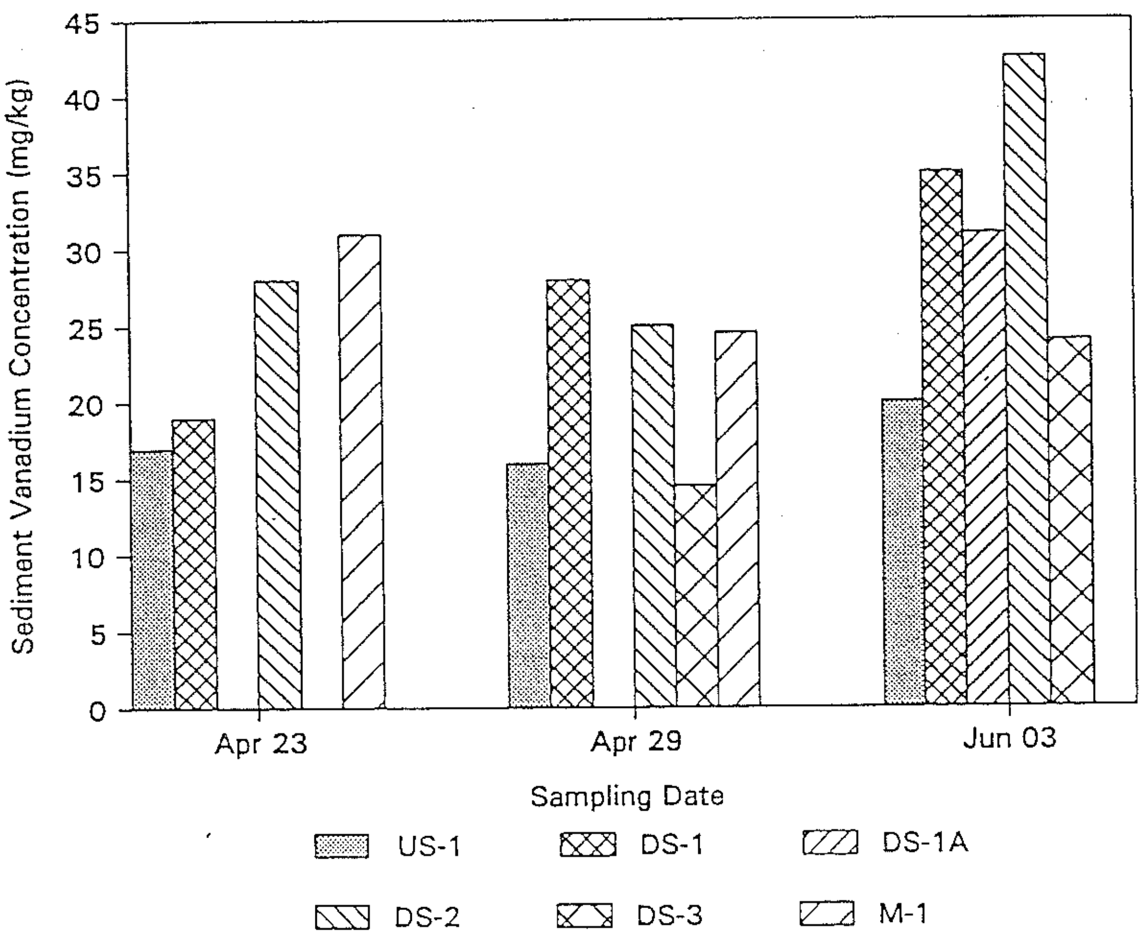


Figure 3-6. Mean concentration of vanadium in sediment samples collected at six sites on three dates following the spill.

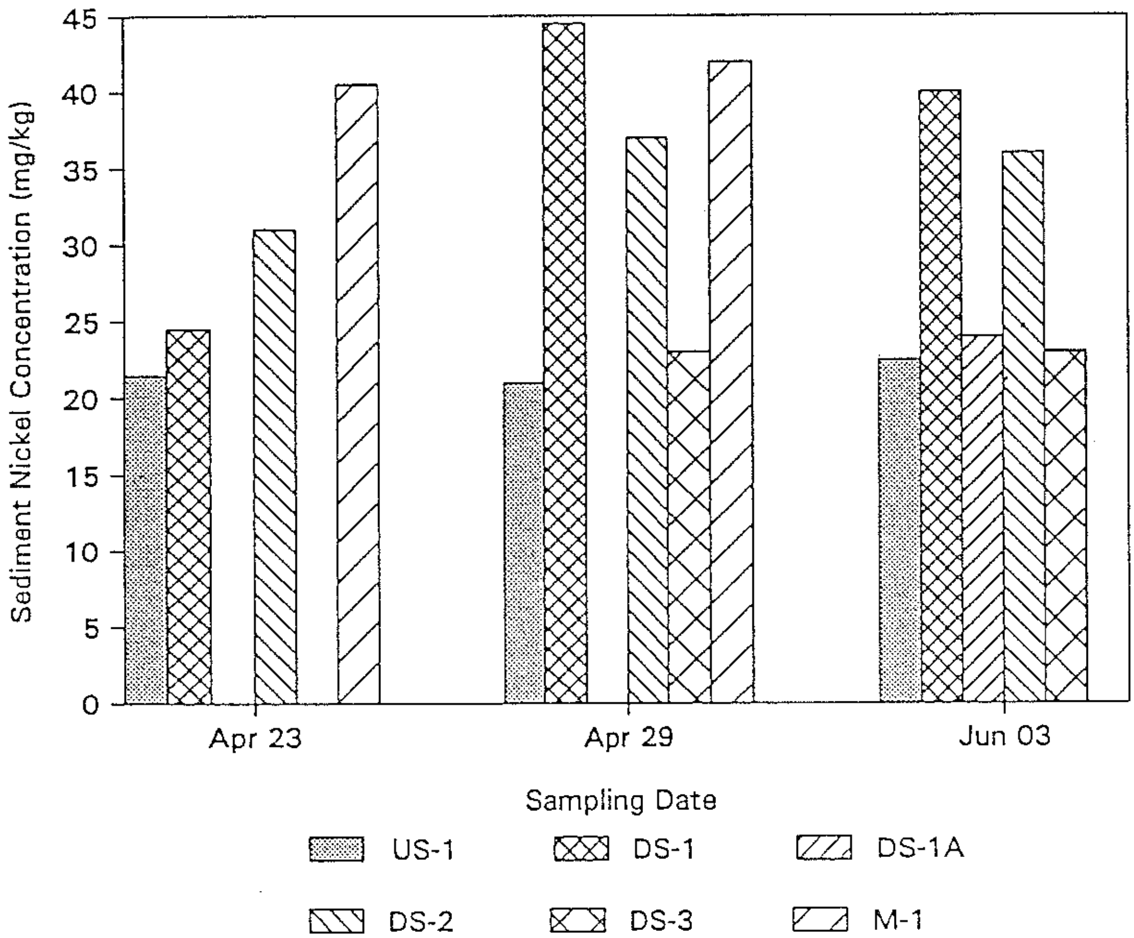


Figure 3-7. Mean concentration of nickel in sediment samples collected at six sites on three dates following the spill.

(Meyer's Ditch) (Figure 3-8). Concentrations of selenium in the sediment were notably higher at all sites during the first sampling period, and decreased dramatically in samples collected during the followup sampling (Figure 3-9). While concentrations at US-1 remained fairly constant throughout all three sampling periods, sediment concentrations at the downstream sites and Meyer's Ditch changed over the course of the study (see Figures 3-5 and 3-6). These changes could be due to resuspension, mixing, and resettling of sediments that can be caused by rainfall and an increase in flows and turbulence in streams. The higher concentration of zinc in the sediments corresponds to the higher levels of zinc in the water column (Figure 3-1). However, high levels of other metals in the sediment (such as selenium) suggest that these metals may also have been at toxic levels in the water, but were not detected due to relatively high method detection levels.

3.2 Biological

3.2.1 Fish Kill

Fish kill counts in Meyer's Ditch and Raccoon Creek indicated that few dead were observed after the acidic material leak. A ground reconnaissance conducted along the entire length of Meyer's Ditch revealed only one dead minnow. A shoreline boat survey in Raccoon Creek from its confluence with Little Raccoon Creek and Lake Erie resulted in 10 dead carp. Since dead carp also were observed by Brent Kuenzli from the Ohio Environmental Protection Agency (Ohio EPA) during a drive along Pickerel Creek, which was not affected by the leak, the dead carp in Raccoon Creek may have resulted from natural causes. If the acidic material had affected fish in Raccoon Creek, it is expected that considerably more fish would have been observed during the survey.

The estimated number of dead fish in Little Raccoon Creek is presented in Table 3-2. By extrapolating the counts in the seven 100-yard segments to the entire 3-mile section of Little Raccoon Creek, an estimated 555 dead fish were present in the study area. The most abundant species in the fish kill estimates included creek chub (*Semotilus atromaculatus*) (195), minnows (Family Cyprinidae) (188), and white sucker (*Catostomus commersoni*) (142). In addition, 30 dead green sunfish (*Lepomis cyanellus*) were present in Little Raccoon Creek. When examining the fish kill counts by individual segments (Figure 2-1; Appendix A, Table A-1), the majority of the dead fish were observed in segments 3, 4, and 5. None of the species observed in the fish kill counts are considered to be gamefish species by Ohio DNR.

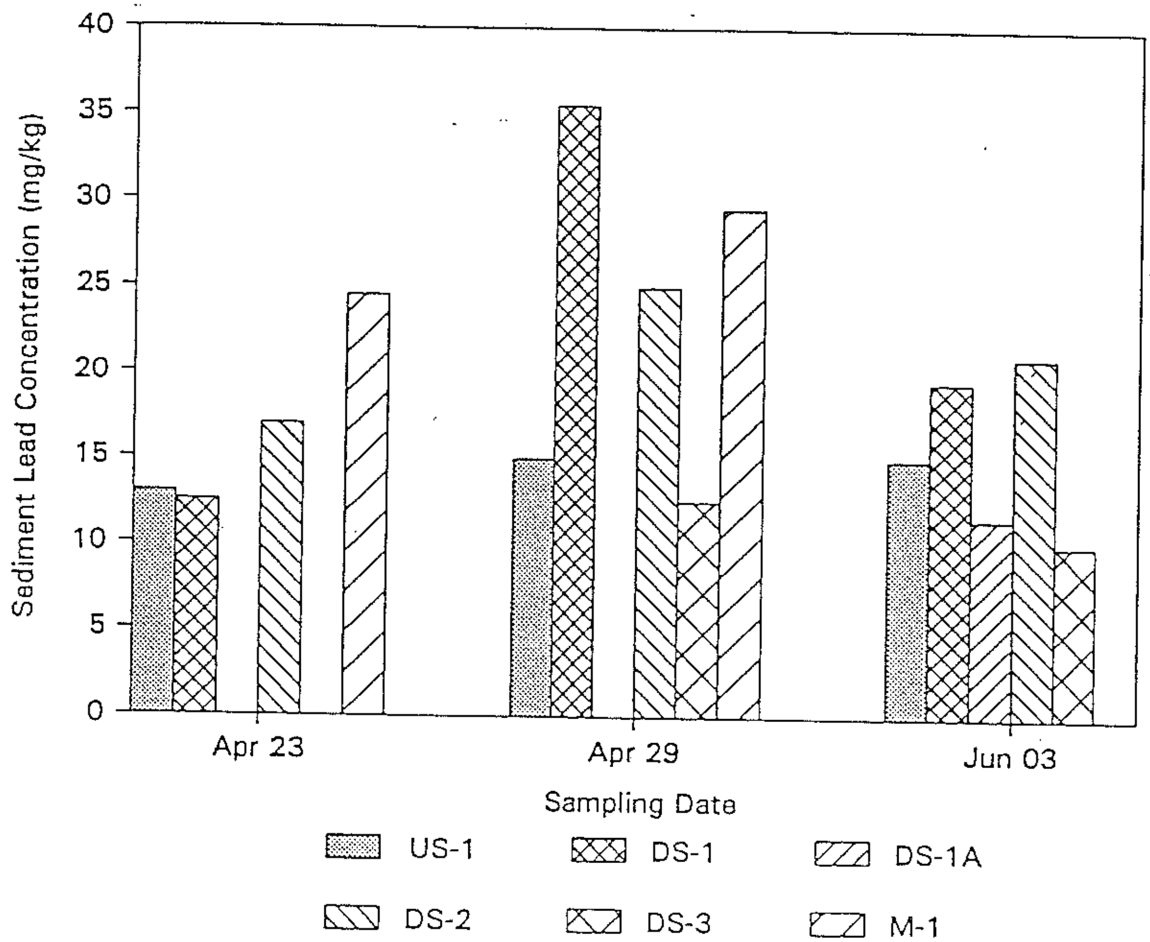


Figure 3-8. Mean concentration of lead in sediment samples collected at six sites on three dates following the spill.

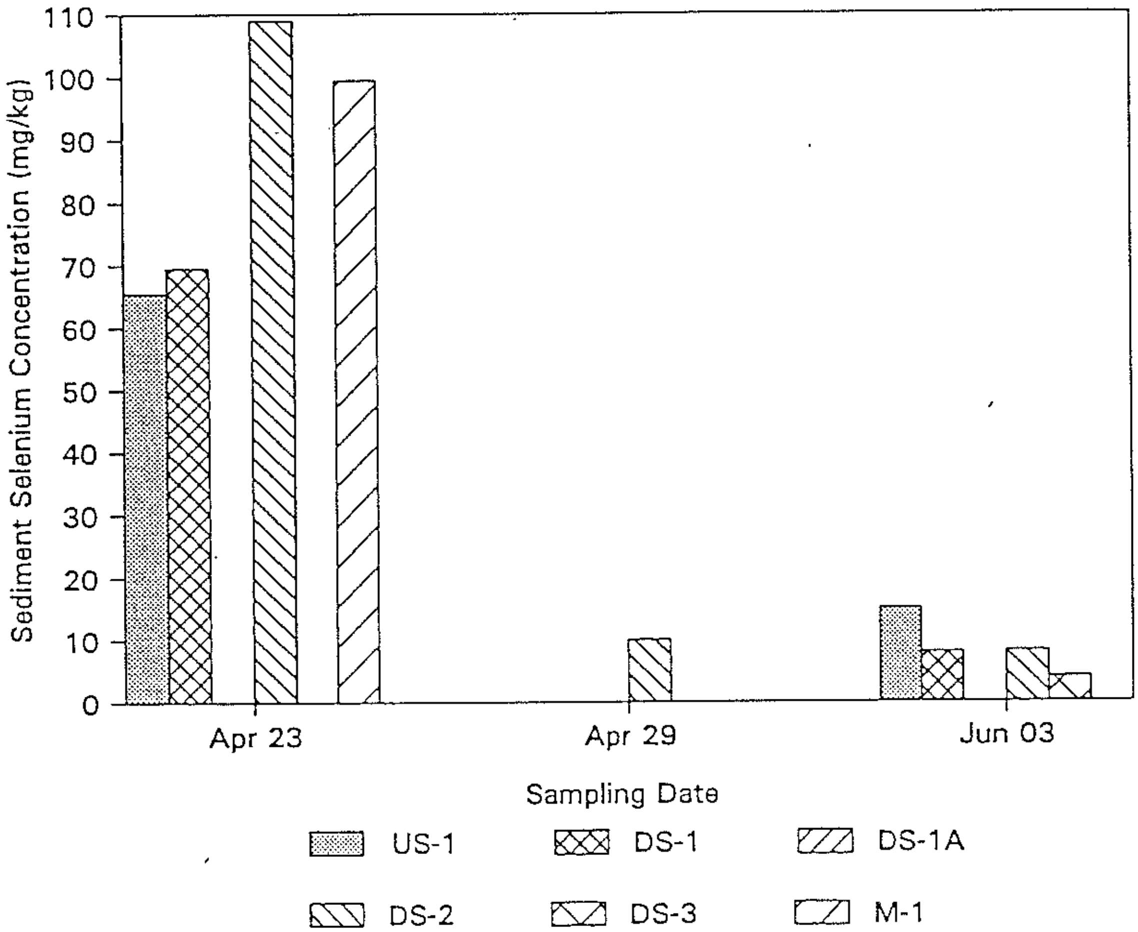


Figure 3-9. Mean concentration of selenium in sediment samples collected at six sites on three dates following the spill.

Table 3-2

Estimated Total Number of Fish
Killed in Little Raccoon Creek

Species	Size (Length) Category	Total Count[1]	Kill Estimate[2]
White Sucker	1 to 3 inches	2	2 x 7.5 = 15
	4 to 6 inches	5	5 x 7.5 = 37.5 = 37
	>12 inches	12	12 x 7.5 = 90
			142
Green Sunfish	2 inches	3	3 x 7.5 = 22.5 = 23
	3 inches	1	1 x 7.5 = 7.5 = 7
			30
Minnows	Not measured	25	25 x 7.5 = 188
Creek Chub	Not measured	26	26 x 7.5 = 195
Total Estimate		74	555

[1]Total number of dead fish observed in the seven 100-yard segments.

[2]Fish kill estimate was calculated using the following "estimate factor":

$$Estimate\ Factor\ (E) = 1{,}760\ yards \times \frac{T}{L}$$

Where: T = Total Length of Stream Affected by Spill.
L = Total Length of Transects Examined.

$$E = 1{,}760\ yards \times \frac{3\ miles}{700\ yards}$$

Where: E = 7.5

3.2.2 Benthic Macroinvertebrates

Most of the organisms collected in Little Raccoon Creek were pollution-tolerant organisms, with tolerance quotients of 108 (USDA 1985) (Table 3-3). Two of the most abundant organisms, *Limnodrilus hoffmeisteri*, a tubificid worm, and *Chironomus* sp., a dipteran midge, are commonly found in soft sediments from both lotic (flowing water) and lentic (lakes and ponds) systems. Macroinvertebrate densities ranged from 1,347 organisms/m^2 at DS-2 to 4,730 organisms/m^2 at DS-1 (Figure 3-10). The mean density at the reference location (US-1) was 1,724 organisms/m^2. The total number of taxa ranged from 7 at DS-2 to 13 at DS-1A (Figure 3-11). The number of taxa does not include empty shells of fingernail clams (Sphaeriidae) and gastropods that were collected in the grab samples. Empty Unionid (large freshwater clams) were also observed along Little Raccoon Creek during the initial visit to the site, suggesting a clam population at some point in the past. There were no significant differences in either density or number of taxa among the sites.

Additional information regarding the macroinvertebrate community structure at the four locations was provided by Shannon Diversity and Evenness. Both Shannon Diversity and Evenness were highest at US-1 (Figures 3-12 and 3-13). These differences in the indices are primarily a result of changes in the composition of the benthic community at sites DS-1 and DS-1A, and the densities of specific taxa. At DS-1, for example, *Limnodrilus hoffmeisteri* and *Chironomus* sp. comprised over 85 percent of the total density. At US-1, on the other hand, *L. hoffmeisteri* comprised only 36 percent of the total density and *Chironomus* sp. was absent. Some species identified at US-1 were not identified at either DS-1 or DS-1A. Those include *Cricotopus bicinctus*, *C. tremulus*, and Ephydridae. Neither amphipods nor isopods were collected at DS-1. Statistical analysis ($\alpha = 0.05$) showed that Shannon Evenness was significantly lower at DS-1, when compared to US-1.

Based on computations of Invertebrate Community Indices according to Ohio EPA (1987), macroinvertebrate communities in Little Raccoon Creek are considered to be low quality. Total scores for the four locations ranged from 0 at DS-2 to 4 at US-1 (Table 3-4). The slightly higher score at the reference location was due to the presence of Tribe Tanytarsini midges. However, the slightly higher score at the reference site does not indicate a substantially higher quality community at this location compared to the downstream locations.

Table 3-3

Mean Benthic Macroinvertebrate Densities Collected in Little Raccoon Creek Using a Petite Ponar Grab

Taxon	Station			
	US-1	DS-1	DS-1A	DS-2
Oligochaeta				
Naididae				
Nais sp.		96.98	32.33	64.65
Tubificidae				
Limnodrilus hoffmeisteri	614.18	3588.08	355.58	312.48
Terrestrial Earthworms			53.88	
Hirudinea				
Glossiphonidae			21.55	
Amphipoda				
Gammaridae				
Gammarus sp.	10.78		96.98	
Isopoda				
Asellidae				
Asellus sp.	21.55		21.55	150.85
Ephemeroptera				
Ephemeridae				
Hexagenia sp.			75.43	
Odonata				
Libellulidae				
Plathemis sp.			10.78	
Coleoptera				
Dytiscidae				
Deronectes sp.		10.78		
Diptera				
Ceratopogonidae	10.78	21.55	10.78	
Chironomidae				
Chironomus sp.		441.78	1282.23	635.73

Table 3-3 (Continued)

Taxon	Station			
	US-1	DS-1	DS-1A	DS-2
Cricotopus bicinctus group	237.05			43.10
Cricotopus tremulus group	129.30			43.10
Cryptochironomus sp.	247.83	118.53	43.10	96.98
Procladius sp.		323.25	64.65	
Rheotanytarsus sp.	258.60	75.43		
Ephydridae	43.10			
Gastropoda[2]				
Pelecypoda				
Sphaeriidae[2]				
Sphaerium sp.	150.85	53.88	43.10	
Total Mean Density:	1724.00	4730.23	2111.90	1346.88
Total Number of Taxa:	10	9	13	7
Shannon Diversity Index[3]:	1.82	0.95	1.45	1.49
Shannon Evenness Index[3]:	0.79	0.43	0.57	0.77

[1]Mean density calculated for four replicates/location.

[2] Some empty shells were found.

[3] Calculated using Natural Log.

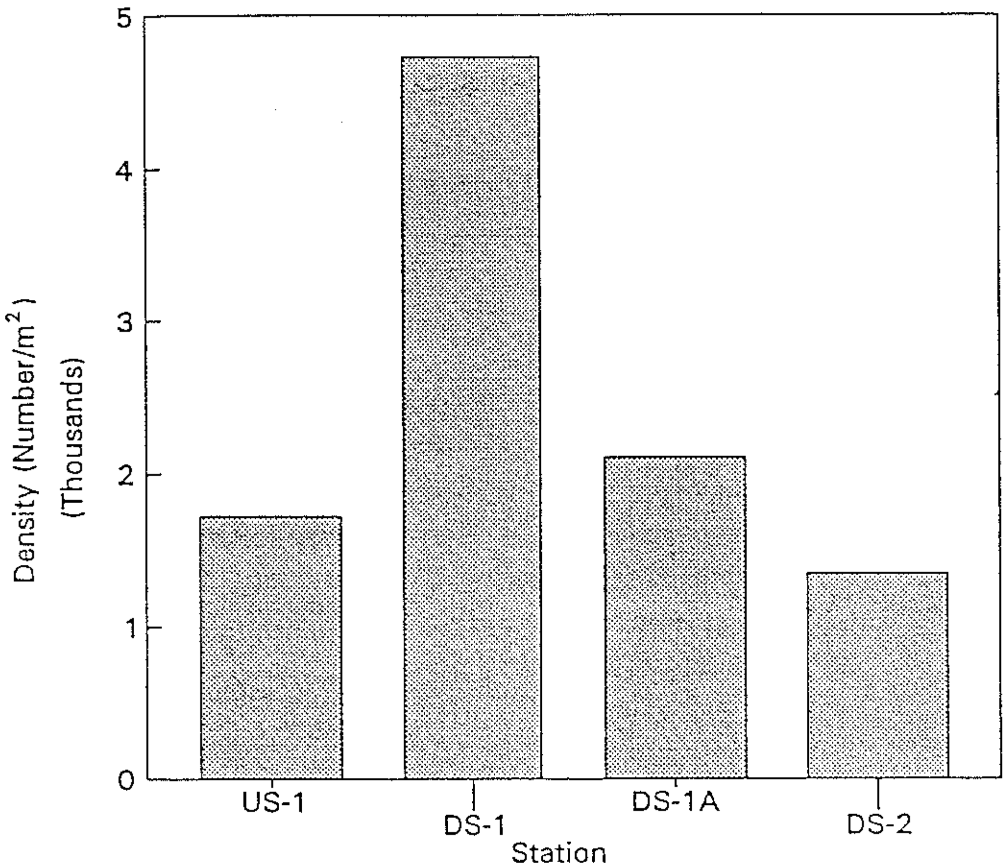


Figure 3-10. Mean density (Number/m^2) of benthic macroinvertebrates collected at each station in Little Raccoon Creek.

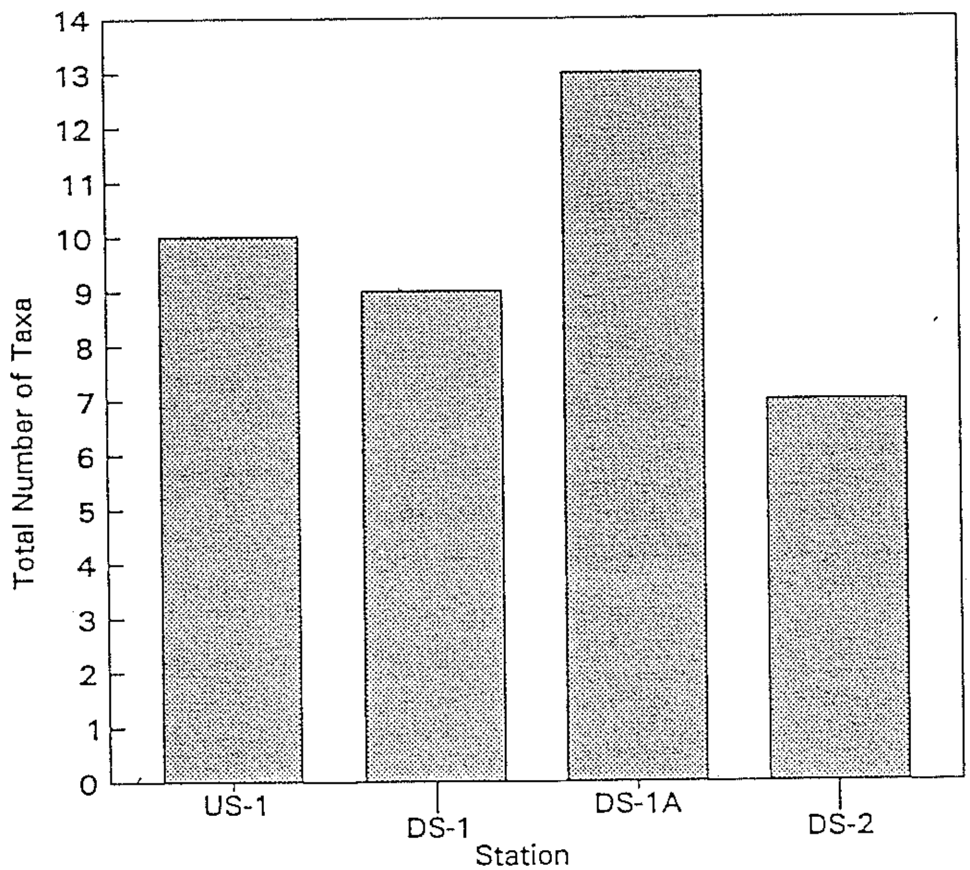


Figure 3-11. Total number of benthic macroinvertebrate taxa collected at each station in Little Raccoon Creek.

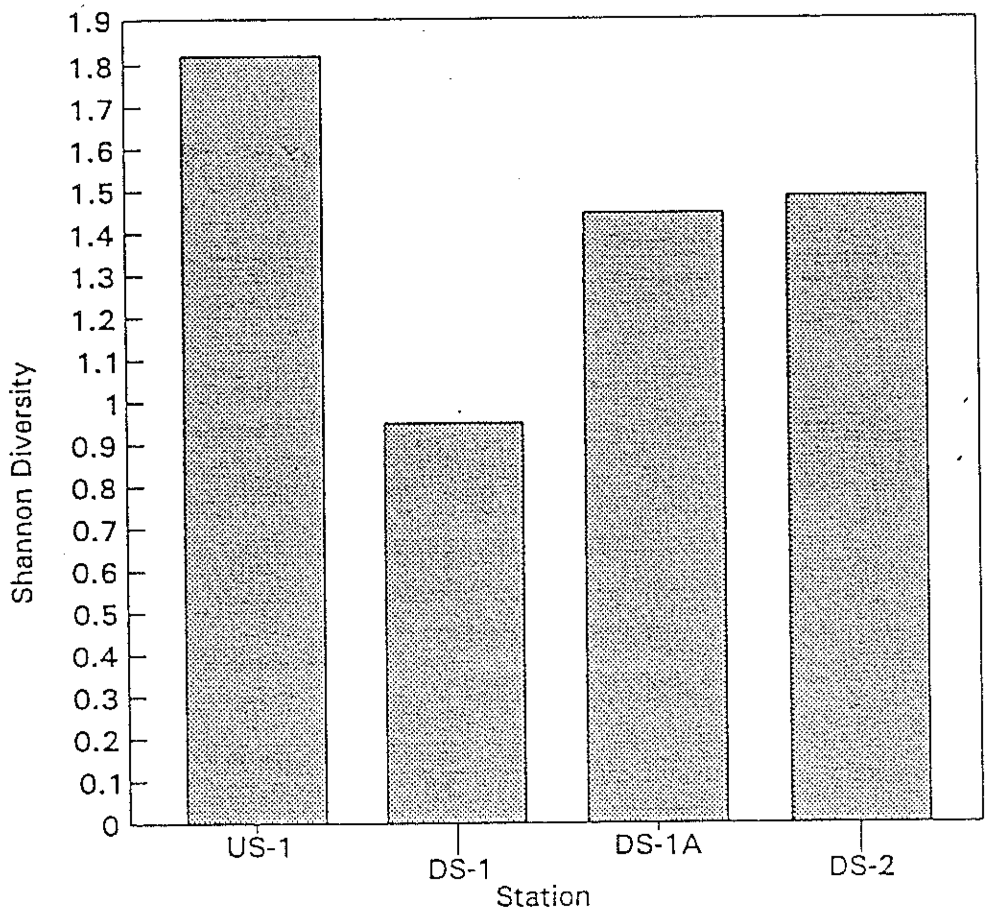


Figure 3-12. Shannon diversity of benthic macroinvertebrate populations collected at each station in Little Raccoon Creek.

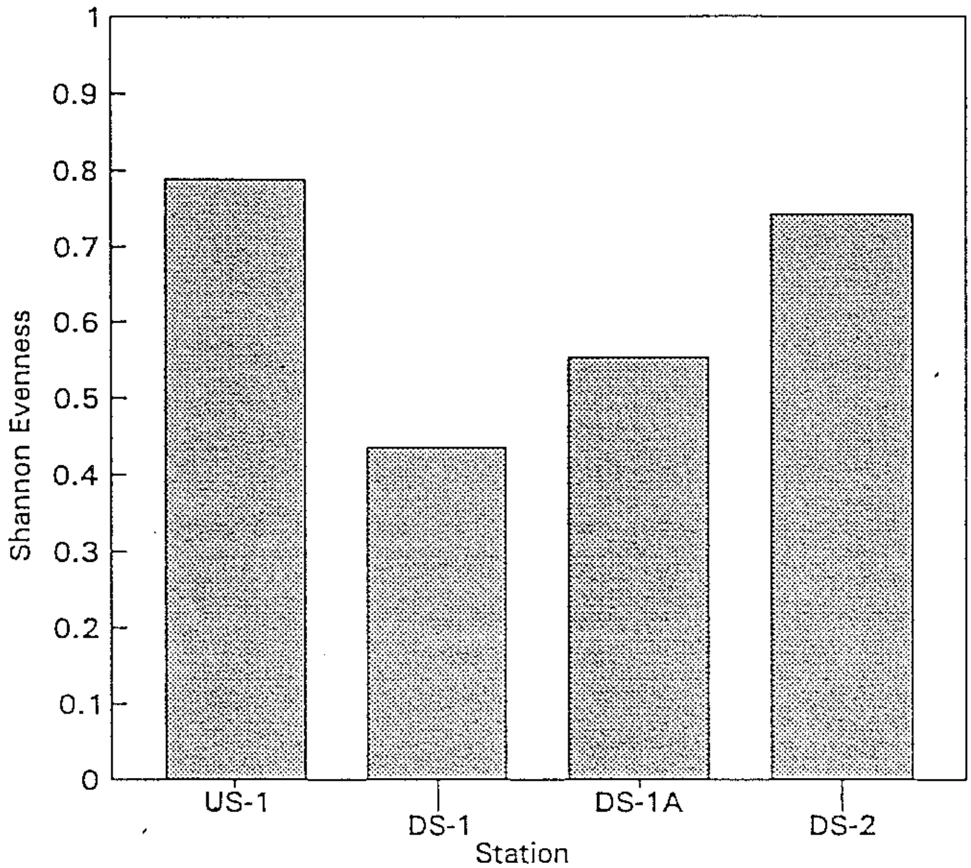


Figure 3-13. Shannon evenness of benthic macroinvertebrate populations collected at each station in Little Raccoon Creek.

Table 3-4

Invertebrate Community Indices for Sampling Locations in Little Raccoon Creek

Parameters	US-1 No.	US-1 Score	DS-1 No.	DS-1 Score	DS-1A No.	DS-1A Score	DS-2 No.	DS-2 Score
1. Total Number of Taxa	10	0	9	0	13	0	7	0
2. Total Number of Mayfly Taxa	0	0	0	0	1	0	0	0
3. Total Number of Caddisfly Taxa	0	0	0	0	0	0	0	0
4. Total Number of Dipteran Taxa	6	0	5	0	4	0	4	0
5. Percent Mayflies	0%	0	0%	0	0%	0	0%	0
6. Percent Caddisflies	0%	0	0%	0	0%	0	0%	0
7. Percent Tribe Tanytarsini Midges	15%	4	2%	2	0%	0	0%	0
8. Percent Other Dipterans and Non-Insects	85%	0	98%	0	100%	0	100%	0
9. Percent Tolerant Organisms	49%	0	87%	0	79%	0	75%	0
10. Total Number of Qualitative Ephemeroptera, Plecoptera, and Trichoptera (EPT) Taxa	0	0	0	0	1	0	0	0
Total Scores		4		2		2		0

3.2.3 Fish Populations

The relatively low water level in Little Raccoon Creek upstream of its confluence with Meyer's Ditch limited its use as a reference site for comparison with location DS-1. For this reason, the emphasis in this assessment was placed on the composition and abundance of fish populations at DS-1 and DS-1A, where dead fish had been observed during the fish kill counts.

Electrofishing surveys conducted in Little Raccoon Creek on June 2, 1993, resulted in a total of nine taxa from the four sampling locations (Table 3-5). The taxa belonged to four families, which included Cyprinidae (minnows and carp), Catostomidae (suckers), Cyprinidontidae (killifishes), and Centrarchidae (sunfishes). The majority of the taxa (five) belonged to Family Cyprinidae. In general, few taxa were collected at the sampling locations. Location DS-1A contained the highest number of taxa with seven, while four taxa were collected at locations DS-1 and DS-2. The reference site, US-1, contained only two fish taxa. Fish distribution in Little Raccoon Creek was different depending on the species. Green sunfish, fathead minnow, and white sucker were found throughout most of the stream, since they were collected at three or four of the locations. The following species were collected only at one location: goldfish and orangespotted sunfish at DS-2, and blackstripe topminnow at DS-1A.

Population estimates in Little Raccoon Creek showed that moderate to high numbers of fish were present. As shown in Table 3-6, the estimated number of fish per acre was 4,646 at DS-1 and 34,902 at DS-1A. The most abundant taxa at these two locations included minnows and green sunfish. Fish numbers at US-1 and DS-2 were considerably lower with estimates of 871 and 1,694 fish per acre, respectively.

Habitat characterization studies conducted at the fish sampling locations provided information concerning the quality of habitat for aquatic communities. In general, the upper 2.5 miles of Little Raccoon Creek contain a relatively small amount of instream cover for fish (i.e., < 5 percent cover for US-1 and 5 to 25 percent for DS-1, DS-1A, and DS-2). The cover is provided by instream debris and woody material, root wads, and overhanging vegetation. The lower 0.5 mile of Little Raccoon Creek contains instream cover that comprises about 25 to 50 percent of the stream bottom. Bottom substrate in Little Raccoon Creek consists of silt, sand, detritus, and clay. Since gravel and cobble substrate are lacking in this stream, substrate does not provide additional fish cover. The four sampling sites also contained relatively shallow pools and glides; riffles were generally absent. The only notable difference in habitat characteristics at DS-1A, where the highest fish numbers were collected, was that the pools and glides were deeper. Habitat characterization forms for studies conducted in Little Raccoon Creek are included in Appendix B.

Table 3-5

Fish Species Collected in Little Raccoon Creek
on June 2, 1993

Common Name	Scientific Name	Sampling Location			
		US-1	DS-1	DS-1A	DS-2
Minnows and Carp	Cyprinidae				
Goldfish	*Carassius auratus*				X
Brassy minnow	*Hybognathus hankinsoni*			X	
Common shiner	*Notropis cornutus*			X	
Fathead minnow	*Pimephales promelas*	X	X	X	
Creek chub	*Semotilus atromaculatus*		X	X	
Suckers	Catostomidae				
White sucker	*Catostomus commersoni*		X	X	X
Killifishes	Cyprinodontidae				
Blackstripe topminnow	*Fundulus notatus*			X	
Sunfishes	Centrarchidae				
Green sunfish	*Lepomis cyanellus*	X	X	X	X
Orange spotted sunfish	*Lepomis humilus*				X
Total Number of Taxa		2	4	7	4

Table 3-6

Fish Population Estimates for Sampling Locations in Little Raccoon Creek

Taxa	Number/Acre			
	US-1	DS-1	DS-1A	DS-2
Goldfish	0	0	0	605
Creek chub	0	0	2,505	0
Minnows	218	2,831	18,731	24
White sucker	0	290	2,178	48
Green sunfish	653	1,307	12,033	895
Orange spotted sunfish	0	0	0	48
Total[1]	871	4,646	34,902	1,694

[1]Total fish population was calculated from total fish collected in two passes using the Seber and LeCren (1967) method rather than the summation of population estimates for all taxa at a sampling location.

3.3 Toxicity Testing

3.3.1 Water Toxicity

All of the water samples collected from the downstream sites (DS-1, DS-2, and DS-3) on April 23 were acute and chronically toxic to *Ceriodaphnia dubia* (Table 3-7). After 48 hours, 100 percent mortality was observed in water collected from these sites. Water collected from US-1 demonstrated a slight chronic effect, with an NOEC of 25 percent stream water.

Less toxicity was observed in the fathead minnow tests. No toxicity was observed in water from US-1; no 48-hour acute toxicity was observed in the downstream samples. However, there was chronic toxicity in all downstream waters, with DS-1 showing the most toxicity to fathead minnows, and DS-3 showing the least.

Toxicity was greatly reduced in samples collected on May 13 (May 17 from DS-1) (Table 3-7). Water from DS-1 still demonstrated some chronic toxicity to *Ceriodaphnia dubia*, and DS-2 water had an NOEC of 12.5 percent for fathead minnows. However, all acute toxicity had disappeared. The control survival (in laboratory water) in the fathead minnow test conducted with DS-3 water collected on May 13 was actually below the 80 percent EPA guideline. However, because survival was similar in all concentrations, this test was accepted as accurate reflection of water toxicity.

3.3.2 Sediment Toxicity

Toxicity of sediment to the amphipod, *Hyalella azteca*, is presented as percent survival (Table 3-8). Survival in the reference sediment was 95 percent, and survival at the three tested sites (US-1, DS-1 and DS-2) was significantly lower than that of the reference sediment. However, when compared against sediment from US-1, survival of *Hyalella azteca* was not significantly lower at DS-1 and DS-2. Therefore, although sediments in Little Raccoon Creek may be toxic to the test organism, the test did not indicate that sediments downstream of Meyer's Ditch were any more toxic than sediments upstream of Meyer's Ditch.

Table 3-7

Toxicity of Stream Water Collected on Two Dates from Little Raccoon and Raccoon Creeks

Endpoint	Date[1]	Station US-1	Station DS-1	Station DS-2	Station DS-3
		Ceriodaphnia dubia			
48-H LC_{50}[2]	April 23	>100[5]	<6.25	<6.25	<6.25
NOEC[3]	April 23	25	<6.25	<6.25	<6.25
IC_{25}[4]	April 23	>100	1.6	1.6	1.6
48-H LC_{50}	May 13	>100	>100	>100	>100
NOEC	May 13	100	6.25	100	100
IC_{25}	May 13	>100	10.2	>100	>100
		Pimephales promelas			
48-H LC_{50}	April 23	>100	>100	>100	>100
NOEC	April 23	100	25	50	100
IC_{25}	April 23	>100	31.7	39.4	94.0
48-H LC_{50}	May 13	>100	>100	>100	>100
NOEC	May 13	100	100	12.5	100
IC_{25}	May 13	>100	>100	100	>100

[1]The second sample from DS-1 was actually collected on May 17; samples from other sites were collected on May 13.

[2]The concentration at which 50 percent of the test organisms die.

[3]No Observed Effects Concentration.

[4]Impact Concentration at which there is a 25 percent reduction in organism performance.

[5]Values are presented as percent stream water; the lower the value, the more toxic the water.

Table 3-8

Toxicity of Stream Sediment to *Hyalella azteca* Collected from Little Raccoon Creek

Sediment/Station	Percent Survival	Significantly Different from Reference Sediment?	Significantly Different from Upstream Control (US-1)?
Reference Sediment	95	NA	NA
US-1 (Control)	63	Yes	NA
DS-1	48	Yes	No
DS-2	65	Yes	No

4.0 DISCUSSION

Analytical chemistry results indicate that several metals were present in the sediments downstream of Meyer's Ditch at concentrations greater than what was seen at US-1, upstream of the confluence. For many of these metals, there were corresponding elevated levels in the water column, primarily in the dissolved, and therefore, bioavailable form. Since concentrations of some elements (e.g., selenium) were also apparently high at US-1, it is possible that some metals were present in stream sediments prior to the leak. However, the higher levels at the downstream sites in samples collected during the first sampling period indicate that some metals, at least, entered Little Raccoon Creek through Meyer's Ditch, probably during the leak. As the pH in Little Raccoon Creek increased following the initial release, metals in the water column precipitated onto sediments (as evidenced by the orange/red precipitate found throughout Little Raccoon Creek). The concentrations measured in the sediments from later sampling periods, while still often high, were different from initial concentrations due, most likely, to one or more storm events which sent large volumes of turbulent water down the creek, thus remixing the existing sediments.

Invertebrates, such as *Ceriodaphnia dubia*, are more sensitive to metals than are most vertebrates, such as the fathead minnow. Although this is also true of other toxicants, the presence of some dissolved metals (such as zinc) at toxic levels strongly suggests that it is, in fact, metal toxicity that affected the test organisms. High concentrations of metals in the sediment suggest that toxic concentrations of other metals, even though they were not detected with the analytical methods used, may have been present in the water column at the time the initial toxicity sample was collected.

Following the rainstorm, and subsequent increases in flow, soon after the leak, concentrations of most metals in the water decreased, as did toxicity. Some metals, such as lead, were higher in the second set of analytical samples; some metals may have become resuspended after the rainstorm. However, it is also possible that lead, perhaps along with other materials, entered Little Raccoon Creek as nonpoint source runoff during the rainstorm. The presence of other materials, possibly nonmetals, may account for the few occurrences of chronic toxicity in the second set of toxicity samples, although those were collected 2 weeks later.

There is no definitive evidence that benthic macroinvertebrate populations were adversely impacted by the leak. Density actually increased downstream of Meyer's Ditch and the number of taxa did not decrease significantly. However, the decrease in Shannon Diversity and

Evenness (which was significant) implies that population structure may have been affected. The extreme toxicity of the water soon after the leak could have had some effects on the benthic community, and probably did affect, in some way, any zooplankton community that may have been supported by Little Raccoon and Raccoon Creeks. However, without having quantitative information on benthic populations prior to the leak, it is not possible to conclude that any differences in macroinvertebrate community structure are due to the acidic material leak. The absence of significant upstream/downstream differences in sediment toxicity indicate that conditions approximately 1 month following the spill were not hazardous to sediment-dwelling organisms.

Regardless of the possible impacts of the spill, the benthic macroinvertebrate communities of Little Raccoon Creek, both upstream and downstream of Meyer's Ditch, are typical of impacted streams. The taxa were pollution-tolerant, and many of the species are very common in polluted systems. The presence of weathered Unionid clam shells implies that the stream may have once supported a much healthier benthic community. However, any degradation occurred long before the April 1993 leak of acidic material.

Observations made after the acidic material leak into the Raccoon Creek drainage indicated that fish were killed in the 3-mile section of Little Raccoon Creek between its confluences with Meyer's Ditch and Raccoon Creek. The fish kill counts in Little Raccoon Creek estimated that approximately 555 fish were killed by the leak. The majority of the fish observed in the fish kill counts were creek chub, minnows, and white sucker. Although some fish were killed due to the material leak, population studies conducted in Little Raccoon Creek indicated that moderate to high numbers of fish were still present in the stream. The only notable change in the post-leak fish population study was that large-sized white suckers were not present. Large white sucker will likely return to Little Raccoon Creek during high water periods prior to spawning in the next several years. Typically, this species moves into small tributary streams to spawn and then returns to larger streams later in the year.

5.0 CONCLUSIONS

5.1 Chemistry

The following conclusions were made regarding the effects of the acidic material leak on water and sediment chemistry:

- Certain metals, in toxic amounts, were released into Little Raccoon Creek as a result of the acidic material leak. Zinc, and possibly selenium, manganese, and other metals were present in a bioavailable form in the water column;

- Sediments contained high levels of several metals; concentrations were generally higher downstream of the confluence with Meyer's Ditch; and

- Dissolved concentrations of previously toxic materials decreased in the second and third sampling periods. Concentrations of some materials increased, particularly during the third sampling period. This may be due to the concentration of ions during low-water conditions.

5.2 Toxicity

The following conclusions were made regarding the toxicity of the stream water and sediment on test organisms:

- Water collected at downstream stations on April 23 was very toxic to *Ceriodaphnia dubia*, and somewhat toxic to fathead minnows. Water collected in Little Raccoon Creek upstream of the confluence with Meyer's Ditch was generally not toxic to these organisms;

- Water collected on May 13 and May 17 (for DS-1 only) was generally not toxic; and

- There was no significant difference in survival of *Hyalella azteca* in sediments from US-1, DS-1, and DS-2.

5.3 Benthic Macroinvertebrates

Based on macroinvertebrate sampling in Little Raccoon Creek, there was no evidence of significant damage on macroinvertebrate communities that could be attributed to the acidic material leak. The following information summarizes the results used in making this conclusion:

- Macroinvertebrate density was highest immediately downstream of Meyer's Ditch;
- The number of taxa and taxonomic composition were similar at the four sampling locations. The number of taxa collected at the reference location was 10, while 7 to 13 taxa were present at the downstream locations;
- Shannon and Evenness Diversity was higher at the reference location. Evenness was significantly lower at DS-1. However, it cannot be determined if this decrease is related to the leak; and
- Invertebrate Community Indices calculated for the four locations indicated that the macroinvertebrate community was considered to be low quality at all locations. Most organisms found at all sites were pollution-tolerant and typical of impacted streams.

5.4 Fish

The conclusion of the fish studies was that no significant damage occurred in the fish populations in the Little Raccoon drainage. The basis for making this conclusion is provided below:

- Based on the fish population studies in Little Raccoon Creek, the fish kill estimate comprised a relatively small portion of the overall population numbers.
- As a result of the relatively high reproductive rates for fish populations in Little Raccoon Creek, fish numbers should return to pre-leak conditions within 1 or 2 years; and
- Large white sucker were removed from Little Raccoon Creek due to this leak. However, spawning movements and development of young suckers in the stream are expected to replenish the large fish.

6.0 REFERENCES

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APPENDIX A

FISH KILL COUNTS IN LITTLE RACCOON CREEK

Table A-1

Fish Kill Counts in Little Raccoon Creek

	Segments[1]							
Species	1	2	3	4	5	6	7	Total
White sucker	0	1	3	5	8	2	0	19
Green sunfish	0	0	3	0	1	0	0	4
Minnows	0	0	4	7	13	1	0	25
Creek chub	0	0	4	4	15	1	2	26
	0	1	14	16	37	4	2	74

[1]Each segment was approximately 100 yards in length; see Figure 2-1 for segment locations.

APPENDIX B

HABITAT CHARACTERIZATION FORMS

0900-0930 hr.

Ohio EPA Site Description Sheet - Fish

QHEI SCORE: [ ]

Stream Little Raccoon Creek RM ____ Date 6/3/93 River Code ____

Location US-1 (100 ft above Myer's Ditch) Crew: Daggett, Patti

1] SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present):

SUBSTRATE SCORE: [ ]

TYPE POOL RIFFLE ✓ silt POOL 20 RIFFLE 20

- ☐☐-BLDER/SLABS[10] ____
- ☐☐-BOULDER [9] ____
- ☐☐-COBBLE [8] ____
- ☐☐-HARDPAN [4] ____
- ☐☐-MUCK [2] ____
- ☐☐-GRAVEL [7] ____ 20
- ☑☐-SAND [6] 40 60
- ☐☐-BEDROCK[5] ____
- ☐☐-DETRITUS[3] 40
- ☐☐-ARTIFIC.[0] ____

TOTAL NUMBER OF SUBSTRATE TYPES: ☐> 4 [2] ☑<= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

SUBSTRATE QUALITY

Substrate Origin (Check all)
- ☐-LIMESTONE [1]
- ☐-TILLS [1]
- ☐-SANDSTONE [0]
- ☐-SHALE [-1]
- ☐-COAL FINES [-2]
- ☐-RIP/RAP [0]
- ☐-HARDPAN [0]

Silt Cover (Check One)
- ☐-SILT HEAVY [-2] ☑-SILT MODERATE [-1]
- ☐-SILT NORMAL [0] ☐-SILT FREE [1]

? Extent Of Embeddness (Check One)
- ☐—EXTENSIVE [-2] ☐—MODERATE[-1]
- ☑—LOW[0] ☐—NONE[1]

COMMENTS Silt covers sand. (about 2-3" silt)

COVER SCORE: [ ]

2] INSTREAM COVER

TYPE (Check All That Apply)

- ☐-UNDERCUT BANKS [1]
- no → ☒-OVERHANGING VEGETATION [1]
- ☐-SHALLOWS (IN SLOW WATER) [1]
- ☐-DEEP POOLS [2]
- ☐-ROOTWADS [1]
- ☐-BOULDERS [1]
- ☐-OXBOWS [1]
- ☐-AQUATIC MACROPHYTES [1]
- ☑-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)
- ☐ - EXTENSIVE > 75% [11]
- ☐ - MODERATE 25-75% [7]
- ☒ - SPARSE 5-25% [3] ← no
- ☒ - NEARLY ABSENT < 5% [1]

COMMENTS: Vegetation cover provided during higher flows; water level was low during survey.

CHANNEL: [ ]

3] CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE)

SINUOSITY
- ☐ - HIGH [4]
- ☒ - MODERATE [3]
- ☐ - LOW [2]
- ☐ - NONE [1]

DEVELOPMENT
- ☐ - EXCELLENT [7]
- ☐ - GOOD [5]
- ☐ - FAIR [3]
- ☒ - POOR [1]

CHANNELIZATION
- ☒ - NONE [6]
- ☐ - RECOVERED [4]
- ☐ - RECOVERING [3]
- ☐ - RECENT OR NO RECOVERY [1]

STABILITY
- ☐ - HIGH [3]
- ☒ - MODERATE [2]
- ☐ - LOW [1]

MODIFICATIONS/OTHER
- ☐ - SNAGGING
- ☐ - RELOCATION
- ☐ - CANOPY REMOVAL
- ☐ - DREDGING
- ☐ - ONE SIDE CHANNEL MODIFICATIONS
- ☐ - IMPOUND.
- ☐ - ISLANDS
- ☐ - LEVEED
- ☐ - BANK SHAPING

COMMENTS: Shallow pools + short in length

RIPARIAN: [ ]

4] RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank)

River Right Looking Downstream

RIPARIAN WIDTH
L R (Per Bank)
- ☒☒-WIDE > 50m [4]
- ☐☐-MODERATE 10-50 [3]
- ☐☐-NARROW 5-10m [2]
- ☐☐-VERY NARROW 1-5m [1]
- ☐☐-NONE[0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY
L R (Most Predominant Per Bank)
- ☒☒-FOREST, SWAMP [3]
- ☐☐-OPEN PASTURE/ ROWCROP[0]
- ☐☐- RESID.,PARK,NEW FIELD [1]
- ☐☐-FENCED PASTURE [1]

L R (Per Bank)
- ☐☐-URBAN OR INDUSTRIAL[0]
- ☐☐-SHRUB OR OLD FIELD[2]
- ☐☐-CONSERV. TILLAGE [1]
- ☐☐-MINING/CONSTRUCTION [0]

None

BANK EROSION
- ☒ ☒-NONE OR LITTLE [3]
- ☐ ☐-MODERATE [2]
- ☐ ☐-HEAVY OR SEVERE[1]

COMMENTS: Minimal erosion along banks.

POOL: [ ]

POOL/GLIDE AND RIFFLE/RUN QUALITY

MAX. DEPTH (Check 1)
- ☐- >1m [6]
- ☐- 0.7-1m [4]
- ☐- 0.4-0.7m [2]
- ☐- < 0.4m [1]
- ☒-<0.2m [Pool = 0]

MORPHOLOGY (Check 1)
- ☐-POOL WIDTH > RIFFLE WIDTH [2]
- ☒-POOL WIDTH = RIFFLE WIDTH [1]
- ☐-POOL WIDTH < RIFFLE W. [0]

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply)
- ☐-TORRENTIAL[-1]
- ☐-FAST[1]
- ☐-MODERATE [1]
- ☒-SLOW [1]
- ☐-EDDIES[1]
- ☐-INTERSTITIAL[-1]
- ☐-INTERMITTENT[-2]

☐-NO POOL[0]

COMMENTS: Few riffles

RIFFLE: [ ]

RIFFLE/RUN DEPTH
- ☐ - GENERALLY > 10 cm,MAX>50 [4]
- ☐ - GENERALLY > 10 cm,MAX<50 [3]
- ☐ - GENERALLY 5-10 cm [1]
- ☒ - GENERALLY < 5 cm [Riffle = 0]

RIFFLE/RUN SUBSTRATE
- ☐-STABLE (e.g.,Cobble, Boulder) [2]
- ☐-MOD. STABLE (e.g.,Pea Gravel) [1]
- ☒-UNSTABLE (Gravel,Sand) [0]

RIFFLE/RUN EMBEDDEDNESS
- ☐-EXTENSIVE [-1] ☐-MODERATE[0]
- ☒-LOW. [1] ☐-NONE[2]

☐-NO RIFFLE[0]

COMMENTS ____

GRADIENT: [ ]

5] Gradient (feet/mile): ____ %POOL: 80 %RIFFLE: 10 %RUN: 10

0930 – 1000 hr

Ohio EPA Site Description Sheet - Fish

QHEI SCORE: ______

Stream: Little Raccoon Creek RM ______ Date: 6/3/97 River Code ______

Location: DS-1 (about 100 ft downstream of Myers Ditch) Crew: Patti, Paggett

1] SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present); SUBSTRATE SCORE: ______

TYPE — POOL RIFFLE ✓ silt — POOL RIFFLE

- ☐☐-BLDER /SLABS[10] ______
- ☐☐-BOULDER [9] ______
- ☐☐-COBBLE [8] ______
- ☐☐-HARDPAN [4] ______
- ☐☐-MUCK [2] ______
- ☐☐-GRAVEL [7] ______
- ☐☒-SAND [6] 30 60
- ☐☐-BEDROCK[5] ______
- ☐☐-DETRITUS[3] ______
- ☐☐-ARTIFIC.[0] ______

SUBSTRATE QUALITY

Substrate Origin (Check all): ☐-LIMESTONE [1] ☐-RIP/RAP [0] ☐-TILLS [1] ☐-HARDPAN [0] ☐-SANDSTONE [0] ☐-SHALE [-1] ☐-COAL FINES [-2]

Silt Cover (Check One): ☒-SILT HEAVY [-2] ☐-SILT MODERATE [-1] ☐ - SILT NORMAL [0] ☐ - SILT FREE [1]

Extent Of Embeddness (Check One): ☐—EXTENSIVE [-2] ☐—MODERATE [-1] ☒—LOW[0] ☐—NONE[1]

TOTAL NUMBER OF SUBSTRATE TYPES: ☐-> 4 [2] ☐— <= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

COMMENTS: Few riffles present

2] INSTREAM COVER COVER SCORE: ______

TYPE (Check All That Apply)

- ☐-UNDERCUT BANKS [1]
- ☐-OVERHANGING VEGETATION [1]
- ☐-SHALLOWS (IN SLOW WATER) [1]
- ☐-DEEP POOLS [2]
- ☒-ROOTWADS [1]
- ☐-BOULDERS [1]
- ☐-OXBOWS [1]
- ☐-AQUATIC MACROPHYTES [1]
- ☒-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)

- ☐ - EXTENSIVE > 75% [11]
- ☐ - MODERATE 25-75% [7]
- ☒ - SPARSE 5-25% [3]
- ☐ - NEARLY ABSENT < 5% [1]

COMMENTS: Low water level limits cover provided by rootwads.

3] CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE) CHANNEL: ______

SINUOSITY: ☐ - HIGH [4] ☐ - MODERATE [3] ☒ - LOW [2] ☐ - NONE [1]

DEVELOPMENT: ☐ - EXCELLENT [7] ☐ - GOOD [5] ☐ - FAIR [3] ☒ - POOR [1]

CHANNELIZATION: ☒ - NONE [6] ☐ - RECOVERED [4] ☐ - RECOVERING [3] ☐ - RECENT OR NO RECOVERY [1]

STABILITY: ☐ - HIGH [3] ☒ - MODERATE [2] ☐ - LOW [1]

MODIFICATIONS/OTHER: ☐ - SNAGGING ☐ - RELOCATION ☐ - CANOPY REMOVAL ☐ - DREDGING ☐ - ONE SIDE CHANNEL MODIFICATIONS ☐ - IMPOUND. ☐ - ISLANDS ☐ - LEVEED ☐ - BANK SHAPING

COMMENTS: Few riffles

4] RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank) RIPARIAN: ______

River Right Looking Downstream

RIPARIAN WIDTH — L R (Per Bank)

- ☐☒-WIDE> 50m [4]
- ☐☐-MODERATE 10-50 [3]
- ☒☐-NARROW 5-10m [2]
- ☐☐-VERY NARROW 1-5m [1]
- ☐☐-NONE[0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY — L R (Most Predominant Per Bank)

- ☐☒-FOREST, SWAMP [3]
- ☒☐-OPEN PASTURE/ ROWCROP[0]
- ☐☐- RESID.,PARK,NEW FIELD [1]
- ☐☐-FENCED PASTURE [1]

L R (Per Bank)

- ☐☐-URBAN OR INDUSTRIAL[0]
- ☐☐-SHRUB OR OLD FIELD[2]
- ☐☐-CONSERV. TILLAGE [1]
- ☐☐-MINING/CONSTRUCTION [0]

None

BANK EROSION

- ☒☒-NONE OR LITTLE [3]
- ☐☐-MODERATE [2]
- ☐☐-HEAVY OR SEVERE[1]

COMMENTS: Bank erosion low.

POOL/GLIDE AND RIFFLE/RUN QUALITY POOL: ______

MAX. DEPTH (Check 1): ☐- >1m [6] ☐- 0.7-1m [4] ☐- 0.4-0.7m [2] ☒- < 0.4m [1] ☐—<0.2m [Pool = 0]

MORPHOLOGY (Check 1): ☐-POOL WIDTH > RIFFLE WIDTH [2] ☒-POOL WIDTH = RIFFLE WIDTH [1] ☐-POOL WIDTH < RIFFLE W. [0]

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply): ☐-TORRENTIAL[-1] ☐-FAST[1] ☐-MODERATE [1] ☒-SLOW [1] ☐-EDDIES[1] ☐-INTERSTITIAL[-1] ☐-INTERMITTENT[-2]

☐-NO POOL[0]

COMMENTS: ______

RIFFLE: ______

RIFFLE/RUN DEPTH: ☐ - GENERALLY >10 cm,MAX>50 [4] ☐ - GENERALLY >10 cm,MAX<50 [3] ☐ - GENERALLY 5-10 cm [1] ☒ - GENERALLY < 5 cm [Riffle = 0]

RIFFLE/RUN SUBSTRATE: ☐-STABLE (e.g.,Cobble, Boulder) [2] ☐-MOD. STABLE (e.g.,Pea Gravel) [1] ☒-UNSTABLE (Gravel,Sand) [0]

RIFFLE/RUN EMBEDDEDNESS: ☐-EXTENSIVE [-1] ☐-MODERATE[0] ☒-LOW. [1] ☐-NONE[2]

☐-NO RIFFLE[0]

COMMENTS ______

GRADIENT: ______

6] Gradient (feet/mile): ______ %POOL: 95 %RIFFLE: 5 %RUN: ______

RD.

Differences between DS-1 & US-1.
DS-1 is slightly deeper with more instream cover. Stream is slightly wider at DS-1. Silt cover is greater @ DS-1. Gradient is lower @ DS-1.

QHEI SCORE: ☐

Ohio EPA Site Description Sheet - Fish

Stream: Little Raccoon Cr. RM ______ Date: 6/3/97 River Code ______

Location: DS-1A Crew: Daggett, Patti

1] SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present); SUBSTRATE SCORE: ☐

TYPE POOL RIFFLE		POOL RIFFLE		SUBSTRATE QUALITY	
☐☐-BLDER /SLABS[10] ____	☐☐-GRAVEL [7] ____ ____		Substrate Origin (Check all)		Silt Cover (Check One)
☐☐-BOULDER [9] ____	☐☐-SAND [6] ____ ____		☐-LIMESTONE [1] ☐-RIP/RAP [0]	☐-SILT HEAVY [-2] ☒-SILT MODERATE [-1]	
☐☐-COBBLE [8] ____	☐☐-BEDROCK[5] ____ ____		☐-TILLS [1] ☐-HARDPAN [0]	☐-SILT NORMAL [0] ☐-SILT FREE [1]	
☐☐-HARDPAN [4] ____	☐☒-DETRITUS[3] ____ 25		☐-SANDSTONE [0]	Extent Of Embeddness (Check One)	
☐☒-MUCK [2] ____ 75	☐☐-ARTIFIC.[0] ____ ____		☐-SHALE [-1]	☐-EXTENSIVE [-2] ☐-MODERATE[-1]	
			☐-COAL FINES [-2]	☒-LOW[0] ☐-NONE[1]	

TOTAL NUMBER OF SUBSTRATE TYPES: ☐-> 4 [2] ☐-<= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates)

COMMENTS: Clay, detritus, & silt substrate. No riffles. Some silt on top of muck (clay)

2] INSTREAM COVER COVER SCORE: ☐

TYPE (Check All That Apply)

☐-UNDERCUT BANKS [1]
☒-OVERHANGING VEGETATION [1]
☐-SHALLOWS (IN SLOW WATER) [1]
☐-DEEP POOLS [2]
☐-ROOTWADS [1]
☐-BOULDERS [1]
☐-OXBOWS [1]
☐-AQUATIC MACROPHYTES [1]
☒-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)
☐ - EXTENSIVE >75% [11]
☐ - MODERATE 25-75% [7]
☒ - SPARSE 5-25% [3]
☐ - NEARLY ABSENT < 5% [1]

COMMENTS: site has more cover than DS-1 but still rated as sparse

3] CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE) CHANNEL: ☐

SINUOSITY	DEVELOPMENT	CHANNELIZATION	STABILITY	MODIFICATIONS/OTHER	
☐ - HIGH [4]	☐ - EXCELLENT [7]	☐ - NONE [6]	☐ - HIGH [3]	☐ - SNAGGING	☐ - IMPOUND.
☐ - MODERATE [3]	☐ - GOOD [5]	? ☒ - RECOVERED [4]	☒ - MODERATE [2]	☐ - RELOCATION	☐ - ISLANDS
☒ - LOW [2]	☐ - FAIR [3]	☐ - RECOVERING [3]	☐ - LOW [1]	☐ - CANOPY REMOVAL	☐ - LEVEED
☐ - NONE [1]	☒ - POOR [1]	☐ - RECENT OR NO RECOVERY [1]		☐ - DREDGING	☐ - BANK SHAPING
				☐ - ONE SIDE CHANNEL MODIFICATIONS	

COMMENTS: may have been channelized

4] RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank) RIPARIAN: ☐

River Right Looking Downstream

RIPARIAN WIDTH
L R (Per Bank)
☐☐-WIDE> 50m [4]
☐☐-MODERATE 10-50 [3]
☐☐-NARROW 5-10m [2]
☒☐-VERY NARROW 1-5m [1]
☐☒-NONE[0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY
L R (Most Predominant Per Bank)
☐☐-FOREST, SWAMP [3]
☐☒-OPEN PASTURE/ ROWCROP[0]
☒☐- RESID.,PARK,NEW FIELD [1] ?
☐☐-FENCED PASTURE [1]

L R (Per Bank)
☐☐-URBAN OR INDUSTRIAL[0]
☐☐-SHRUB OR OLD FIELD[2]
☐☐-CONSERV. TILLAGE [1]
☐☐-MINING/CONSTRUCTION [0]
— None

BANK EROSION
☐ ☒-NONE OR LITTLE [3]
☐ ☐-MODERATE [2]
☐ ☐-HEAVY OR SEVERE[1]

COMMENTS: ______

POOL/GLIDE AND RIFFLE/RUN QUALITY POOL: ☐

MAX DEPTH (Check 1)
☐- >1m [6]
☐- 0.7-1m [4]
☒ 0.4-0.7m [2]
☐- < 0.4m [1]
☐-<0.2m (Pool = 0)

MORPHOLOGY (Check 1)
☐-POOL WIDTH > RIFFLE WIDTH [2]
☐-POOL WIDTH = RIFFLE WIDTH [1]
☒-POOL WIDTH < RIFFLE W. [0]
no riffles

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply)
☐-TORRENTIAL[-1]
☐-FAST[1]
☐-MODERATE [1]
☒-SLOW [1]
☐-EDDIES[1]
☐-INTERSTITIAL[-1]
☐-INTERMITTENT[-2]

☐-NO POOL[0]

COMMENTS: ______

RIFFLE: ☐

RIFFLE/RUN DEPTH
☐ - GENERALLY >10 cm,MAX>50 [4]
☐ - GENERALLY >10 cm,MAX<50 [3]
☐ - GENERALLY 5-10 cm [1]
☒ - GENERALLY < 5 cm [Riffle = 0]

RIFFLE/RUN SUBSTRATE
☐-STABLE (e.g.,Cobble, Boulder) [2]
☐-MOD. STABLE (e.g.,Pea Gravel) [1]
☐-UNSTABLE (Gravel,Sand) [0]
Not applicable

RIFFLE/RUN EMBEDDEDNESS
☐-EXTENSIVE [-1] ☐-MODERATE[0]
☒-LOW. [1] ☐-NONE[2]
☐-NO RIFFLE[0]

COMMENTS: no riffles

GRADIENT: ☐

6] Gradient (feet/mile): ______ %POOL: 100 %RIFFLE: ______ %RUN: ______

QHEI SCORE: ☐

Ohio EPA Site Description Sheet - Fish

RM ______ Date 6/3/97 River Code ______

Stream Little Raccoon Creek Crew: Daggett, Patti

Location RS-2 (about 100 ft upstream of Raccoon Cr. confluence

SUBSTRATE SCORE: ☐

1] SUBSTRATE (Check ONLY Two Substrate TYPE BOXES; Check all types present);

TYPE — POOL RIFFLE

☐☐-BLDER/SLABS[10] ___ ___ ☐☐-GRAVEL[7] ___ ___
☐☐-BOULDER[9] ___ ___ ☐☐-SAND[6] ___ ___
☐☐-COBBLE[8] ___ ___ ☐☐-BEDROCK[5] ___ ___
☐☐-HARDPAN[4] ___ ___ ☐☐-DETRITUS[3] ___ ___
☒☒-MUCK[2] 100 ___ ☐☐-ARTIFIC[0] ___ ___

TOTAL NUMBER OF SUBSTRATE TYPES: ☐-> 4 [2] ☐-<= 4 [0]

NOTE: (Ignore sludge that originates from point-sources; score is based on natural substrates) Clay & black organic matter dominated substrate

SUBSTRATE QUALITY

Substrate Origin (Check all): ☐-LIMESTONE [1] ☐-RIP/RAP [0] ☐-TILLS [1] ☐-HARDPAN [0] ☐-SANDSTONE [0] ☐-SHALE [-1] ☐-COAL FINES [-2]

Silt Cover (Check One): ☐-SILT HEAVY [-2] ☒-SILT MODERATE [-1] ☐-SILT NORMAL [0] ☐-SILT FREE [1]

Extent Of Embeddness (Check One): ☐-EXTENSIVE [-2] ☐-MODERATE [-1] ☒-LOW [0] ☐-NONE [1]

COMMENTS No riffles present. Small amount of silt over muck.

COVER SCORE: ☐

2] INSTREAM COVER

TYPE (Check All That Apply)

☐-UNDERCUT BANKS [1] ☐-DEEP POOLS [2] ☐-OXBOWS [1]
☒-OVERHANGING VEGETATION [1] ☒-ROOTWADS [1] ☐-AQUATIC MACROPHYTES [1]
☐-SHALLOWS (IN SLOW WATER) [1] ☐-BOULDERS [1] ☒-LOGS OR WOODY DEBRIS [1]

AMOUNT (Check ONLY One or check 2 and AVERAGE)

☐-EXTENSIVE > 75% [11]
☒-MODERATE 25-75% [7]
☐-SPARSE 5-25% [3]
☐-NEARLY ABSENT < 5% [1]

COMMENTS: Depths ranged from about <0.5 to 2.5 ft; cover provided by overhanging veg., grasses, & instream deb

CHANNEL: ☐

3] CHANNEL MORPHOLOGY: (Check ONLY One PER Category OR check 2 and AVERAGE)

SINUOSITY: ☐-HIGH [4] ☒-MODERATE [3] ☐-LOW [2] ☐-NONE [1]

DEVELOPMENT: ☐-EXCELLENT [7] ☐-GOOD [5] ☐-FAIR [3] ☒-POOR [1]

CHANNELIZATION: ☒-NONE [6] ☐-RECOVERED [4] ☐-RECOVERING [3] ☐-RECENT OR NO RECOVERY [1]

STABILITY: ☐-HIGH [3] ☒-MODERATE [2] ☐-LOW [1]

MODIFICATIONS/OTHER: ☐-SNAGGING ☐-RELOCATION ☐-CANOPY REMOVAL ☐-DREDGING ☐-ONE SIDE CHANNEL MODIFICATIONS ☐-IMPOUND. ☐-ISLANDS ☐-LEVEED ☐-BANK SHAPING

COMMENTS: 2 bends in about 500 ft section

RIPARIAN: ☐

4] RIPARIAN ZONE AND BANK EROSION - (check ONE box per bank or check 2 and AVERAGE per bank)

River Right Looking Downstream

RIPARIAN WIDTH — L R (Per Bank)

☒☐-WIDE > 50m [4]
☐☐-MODERATE 10-50 [3]
☐☐-NARROW 5-10m [2]
☐☒-VERY NARROW 1-5m [1]
☐☐-NONE [0]

EROSION/RUNOFF - FLOOD PLAIN QUALITY — L R (Most Predominant Per Bank)

☒☐-FOREST, SWAMP [3]
☐☒-OPEN PASTURE/ROWCROP [0]
☐☐-RESID.,PARK,NEW FIELD [1]
☐☐-FENCED PASTURE [1]

L R (Per Bank)

☐☐-URBAN OR INDUSTRIAL [0]
☐☐-SHRUB OR OLD FIELD [2]
☐☐-CONSERV. TILLAGE [1]
☐☐-MINING/CONSTRUCTION [0]

None

BANK EROSION

☒ ☐-NONE OR LITTLE [3]
☐ ☐-MODERATE [2]
☐ ☐-HEAVY OR SEVERE [1]

COMMENTS: ______

POOL: ☐

POOL/GLIDE AND RIFFLE/RUN QUALITY

MAX. DEPTH (Check 1): ☐->1m [6] ☒-0.7-1m [4] ☐-0.4-0.7m [2] ☐-<0.4m [1] ☐-<0.2m [Pool = 0]

MORPHOLOGY (Check 1): ☐-POOL WIDTH > RIFFLE WIDTH [2] ☐-POOL WIDTH = RIFFLE WIDTH [1] ☒-POOL WIDTH < RIFFLE W. [0]

POOL/RUN/RIFFLE CURRENT VELOCITY (Check All That Apply): ☐-TORRENTIAL [-1] ☐-FAST [1] ☐-MODERATE [1] ☒-SLOW [1] ☐-EDDIES [1] ☐-INTERSTITIAL [-1] ☐-INTERMITTENT [-2]

☐-NO POOL [0]

COMMENTS: No riffles

RIFFLE: ☐

RIFFLE/RUN DEPTH: ☐-GENERALLY >10 cm, MAX>50 [4] ☐-GENERALLY >10 cm, MAX<50 [3] ☐-GENERALLY 5-10 cm [1] ☒-GENERALLY < 5 cm [Riffle = 0]

RIFFLE/RUN SUBSTRATE: ☐-STABLE (e.g., Cobble, Boulder) [2] ☐-MOD. STABLE (e.g., Pea Gravel) [1] ☐-UNSTABLE (Gravel, Sand) [0]

Not applicable

RIFFLE/RUN EMBEDDEDNESS: ☐-EXTENSIVE [-1] ☐-MODERATE [0] ☒-LOW. [1] ☐-NONE [2]

☐-NO RIFFLE [0]

COMMENTS ______

GRADIENT: ☐

6] Gradient (feet/mile): ______

%POOL: 100 %RIFFLE: ______ %RUN: ______

pool/glide no riffles.

ENSR

ENSR Consulting and Engineering

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